

Sonoluminescence from Alkaline-Earth Metals in Sulfuric Acid 硫酸中アルカリ土類金属からのソノルミネッセンス

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1. Introduction

Sonoluminescence (SL) is the phenomenon of light emission from acoustic cavitation bubbles at collapse, where acoustic energy is concentrated by 12 orders of magnitude to create flashes of light. Extremely high-intensity SL found in sulfuric acid¹⁾ also provided intense emission from alkali-metal atoms during single bubble SL (SBSL),²⁾ which was observed for the first time during SBSL, and its spatial separation observed during multibubble SL (MBSL).^{3,4)} The alkali-metal atom emission with stroboscopic observation of the corresponding bubble dynamics have given further insight into the mechanism of how nonvolatile metal cations get heated in a collapsing bubble. The results supported an injected droplet model, where nanodroplets of liquid are nebulized into the interior of the bubble by capillary waves on or microjets from the bubble surface. However, the mechanism of the excitation of metal ions inside the bubble is still unclear.

SL from alkaline-earth metals may provide further information about the excitation mechanism because the valence of ions is different from that of alkali metals. As for SL from alkaline-earth metals, Taylor and Jarman⁵⁾ reported neutral Ca* emission at 422.7 nm and two bands of CaOH at about 547.0 and 612.0 nm in aqueous calcium chloride solutions. Furthermore, they reported that the usually strong emission lines of monovalent cation Ca⁺ at 396.9 and 393.4 nm were found in an argon-saturated solution irradiated at only 500 kHz and they supposed that the emission may have been present in other cases (16 kHz for their experiment) but were difficult to observe since they occurred so close to the peak of the continuum, although they did not show the profile of the spectrum for Ca emission. Arakeri⁶⁾ showed the spectrum from argon saturated calcium chloride ethylene glycol solution at 31.25 kHz, where Ca⁺ was vague, in spite of no continuum peak appeared in the solution. Sakurada and Choi⁷⁾ reported the detailed spectra for argon or krypton saturated aqueous calcium chloride solution at 140 kHz, where the small peaks of Ca⁺ line seemed to exist on the continuum.

In the present study, we report SL from strontium and barium as well as calcium sulfate

95% sulfuric acid solutions. The SL spectra of Sr and Ba emissions are first observed as long as we know. The characteristics of the spectra is that there exist the excited cation emissions, whose intensities seem to be much higher than those in flame spectra.

2. Experimental

Ultrasonic irradiation was performed using a commercial ultrasonic horn (Sonics and Materials, VCX 600 Vibra Cell) at 20 kHz with a 1 cm diameter Ti horn immersed in 95 wt % sulfuric acid in a 250 mL quartz round bottom flask after sparging with Ar for 2 hours. The MBSL spectra were collected with a 0.32-m monochromator (Horiba, Triax320) equipped with a triple grating turret on which 300 gr/mm grating blazed at 250 nm, 1200 gr/mm grating blazed at 750 nm and 1200 gr/mm grating blazed at 330 nm were mounted and fitted with a 1024 x 256 pixel liquid nitrogen-cooled CCD camera (Horiba, CCD-3000). A slit width in the range of 0.1 – 1.0 mm was used to acquire spectra.

The sulfuric acid (H₂SO₄) used was of normal grade (95.0-97.0%) and calcium, strontium and barium sulfate was of pure grade (min. 99.0%). The concentrations of sulfates were 0.3 mol/L.

3. Results and Discussion

Figure 1 shows photographs of MBSL in

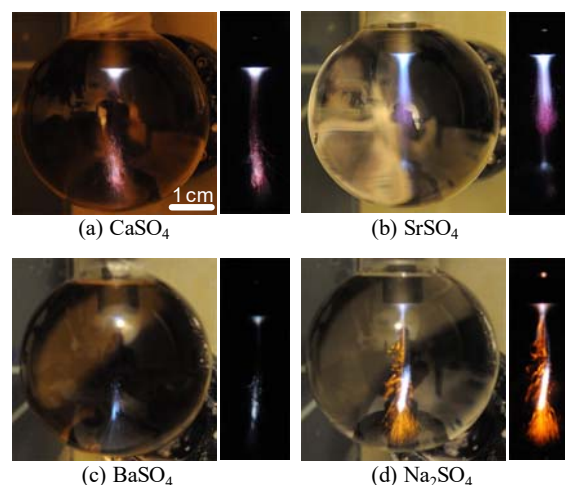


Fig. 1. Photos of SL in 0.3 M (a) CaSO₄, (b) SrSO₄ and (c) BaSO₄ solutions with (d) Na₂SO₄ for comparison.

alkaline-earth sulfate sulfuric acid solutions. The left side photos were taken with flashlight and right side ones in the dark. As shown in Fig. 1, blue-white emission region near the horn tip and reddish orange, red and orange emission one in (a), (b) and (d) are spatially separated, although green emission is not so clear in (c). The emission region of alkaline-earth metals seems to be similar to that of alkali metal of Na.

Because the alkaline-earth metal emission region could be seen by the different color from blue-white one, the spectrum in the region was collected for each metal solution. The uncorrected MBSL spectra in the regions for calcium, strontium and barium are shown in Figs. 2-4, respectively. The excited neutral atom emission and metal hydroxide molecular emission are significantly observed in all the case, which are similar to those in flame.⁸⁾ However, the excited cation emission lines are also observed, where the relative intensities seem to be much higher than those in flame spectra.⁸⁾ This can imply that extremely high temperatures and pressures inside cavitation bubbles exist. On the other hand, it can be excited not by thermally but by electron or some other atom or molecular impact. It should be noted that emission from excited monovalent cation cannot be observed in alkali metal salt solutions and similarly emission from excited divalent cation is not observed in alkaline-earth metal salt solutions, in spite of original ionic valence in the solutions.

4. Conclusion

Multibubble sonoluminescence spectra from alkaline-earth metals of calcium, strontium and barium sulfates in sulfuric acid solutions were observed by a 20 kHz ultrasonic horn. The emission region of the line and band spectra associated with the alkaline-earth metal was spatially separated from the continuum, similarly to those of alkali metals. The spectra showed intense emission from the excited state of the neutral atom, monovalent cation and metal hydroxide molecular. The relative intensity of monovalent cation emission seemed to be much higher than that in flame, which can imply the extreme environment inside cavitation bubble or not thermal excitation of monovalent cation.

References

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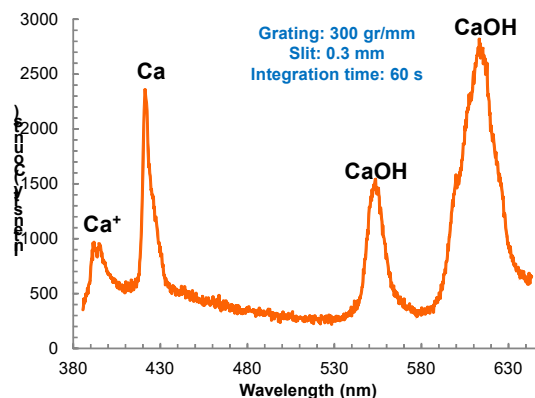


Fig. 2. Spectrum of multibubble sonoluminescence in 0.3 M $\text{CaSO}_4\text{-H}_2\text{SO}_4$ solution under Ar irradiated by an ultrasonic horn at 20 kHz.

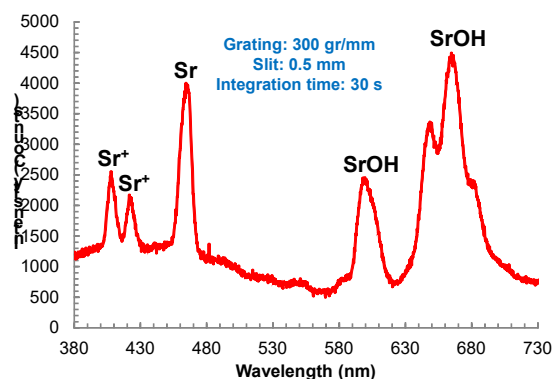


Fig. 3. Spectrum of multibubble sonoluminescence in 0.3 M $\text{SrSO}_4\text{-H}_2\text{SO}_4$ solution under Ar irradiated by an ultrasonic horn at 20 kHz.

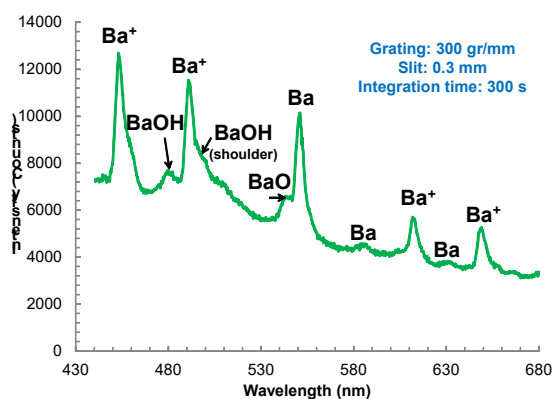


Fig. 4. Spectrum of multibubble sonoluminescence in 0.3 M $\text{BaSO}_4\text{-H}_2\text{SO}_4$ solution under Ar irradiated by an ultrasonic horn at 20 kHz.