Spectra of surface-enhanced Raman scattering of nanocluster NaXe

JIACHANG LIANG*, ZHI LIU, LIPING ZHANG
College of Science, Civil Aviation University of China, Tianjin 300300, People's Republic of China
E-mail: jch_liang@yahoo.com

The integrated ultraviolet (UV)-micro-laser-matrix can be expected, if the novel nanomaterial with a matrix distribution can emit UV radiation and easily inverses the population between its ground and excited states. Solid NaXe nanoclusters should belong to such a nanomaterial.

Metallic Na colloids of nanometer size have been formed as the results of the aggregations of F centers in heavily irradiated NaCl [1]. It has been indicated by the measurements of transmission electron microscopy (TEM) that alkali atoms, including Na and K, in alkali metal colloids retain their original face centered cubic (fcc) positions within the alkali halide matrix and that their lattice parameters are not far different from their host matrix [2]. It has been also evidenced by TEM and selected-area electron diffraction experiments that noble-gas ions implanted into metals and magnesium oxide can be trapped and solid noble-gas inclusion can be formed [3]. Their positions have been found to be fccs in fcc matrix [3]. It has been also demonstrated by our former experiments [4, 5] that the novel solid NaXe can be prepared under the appropriate conditions of xenon ion implantation into NaCl samples and a strong 355 nm-UV-radiation emission can be observed. In this paper, the surface-enhanced Raman scattering (SERS) spectra of nanocluster NaXe in NaCl are measured at room temperature and their characteristics are discussed.

In the experiment, pure NaCl powder, in which the grain diameters are smaller than 53 μm, is pressed to disks as samples. Xenon ions are implanted at 10^{-6} Torr by using an accelerating voltage of 200 kV. The xenon ion flux is 5×10^{17} ions/cm^2. Under this implantation condition, solid NaXe nanoclusters with blue color are formed through the interaction between solid Xe and metallic Na colloids in xenon-ion–implanted NaCl samples. The sizes of solid NaXe nanoclusters are measured to be within 80 nm by scanning electron microscopy (Hitachi S-3500N).

The Raman-scattering is often enhanced by the colloids formed on the surface of the sample. This process is called SERS [6]. These SERS spectra can provide information about the nature and geometry of the colloids in samples. Therefore, low-frequency Raman-scattering spectra are used to study the colloidal structure in our experiments. The SERS spectra of NaCl samples containing solid NaXe nanoclusters are measured by using a Renishaw micro spectrometer system 1000. By means of Leica micro system, the stimulating light of 632.8 nm, produced by He–Ne laser moder-127, is led to the surface of samples. The scattering light is collected by the same micro system, the diameter of its focal spot is 0.1 μm and measuring time is 30 s. All measurements are done at room temperature.

The SERS spectra of 200 keV xenon-ion-implaned NaCl samples are measured at room temperature and shown in Figs 1 and 2.

As shown in Fig. 1, the SERS peaks (i.e., Raman frequency shifts) of solid NaXe nanoclusters with dark blue color are located at 95, 108, 125, 146, 200, 224, and 320 cm^{-1}, these peaks are superimposed on the wide peak near 170 cm^{-1}, which full-width at half-maximum reaches ±60 cm^{-1}. The wide peak is the result of the dissociation of the ground state of solid NaXe.

These peak values of SERS, produced by the dissociation of nanocluster NaXe, are very close to the critical point phonon frequencies of NaCl lattice in the second-order Raman scattering [6, 7], as listed in

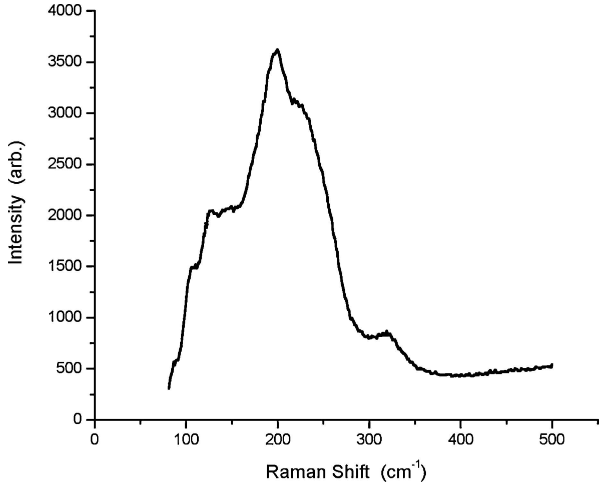

Figure 1 SERS spectrum of solid NaXe nanoclusters with dark blue color in 200 keV xenon-ion-implanted NaCl sample measured at room temperature.

---

* Author to whom all correspondence should be addressed.

0022-2461
DOI: 10.1007/s10853-005-4225-4

TABLE I Phonon peaks (i.e., Raman frequency shifts) of Na colloids in NaCl at 78 K and in NaXe nanoclusters at room temperature, respectively

Phonon peaks of Na collids in NaCl at 78 K (cm^{-1})	Raman frequency shifts of Na collids in NaXe at room temperature (cm^{-1})	Difference of peak value (cm^{-1})
100	95	−5
115	108	−7
134	125	−9
154	146	−8
205	200	−5
230	224	−6
	320	

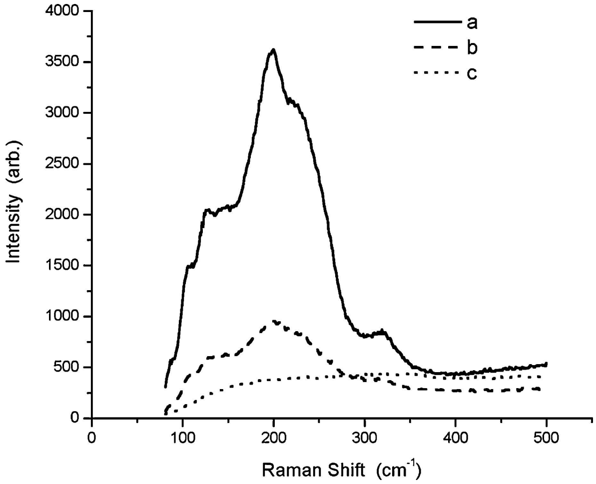

Figure 2 SERS spectra of solid NaXe nanoclusters with dark blue, light blue, and white color, respectively, in 200 keV xenon-ion-implanted NaCl sample measured at room temperature.

Table I. This table shows that the difference of peak values between Na colloids, produced by NaCl and NaXe, equals about 3–7%, respectively. This should suggest that solid NaXe may retain fcc position within the host NaCl matrix, as shown by Norton *et al.,* [3].

As shown in Fig. 1 and Table I, Raman frequency shift of 320 cm^{-1}, which is higher than the phonon cutoff frequency 262 cm^{-1} in NaCl [6], should belong to the phonon frequency of nano-Xe produced by the dissociation of nanocluster NaXe.

Fig. 2 shows that higher concentration of NaXe nanoclusters, which displays dark blue color, has the higher intensity of SERS. The lower concentration of NaXe nanoclusters, which displays light blue color, has the lower intensity of SERS. And SERS disappears for the sample with white color, in which there is no NaXe nanocluster.

Now, it is clear that the solid NaXe has easily dissociated ground state and stable excited states to emit short wavelength radiations, including 355 nm-UV-emission [5]. Therefore, the population inversion between its ground and excited states can be put into practice.

In ab initio calculations the Gaussian 98 program packages with configuration interaction-singlets [8] are used for the structure calculation and optimization of NaXe. The predicted ground state energy 151 cm^{-1} is also consistent with the dissociation energy of NaXe demonstrated by the wide peak, as shown in Fig. 1. For NaXe the bond distance, dipole, molecular orbital, charge transition from Xe to Na and chemical shifts of ^{23}Na and ^{129}Xe in NaXe relative to xenon and ^{23}Na in NaCl are also caculated respectively.

References

1. J. R. W. WEERKAMP *et al.*, *Phys. Rev. B* **50** (1994) 9781.
2. L. W. HOBB *et al.*, *Nature* **252** (1974) 383.
3. M. G. NORTON *et al.*, *Phys. Rev. B* **43** (1991) 9291.
4. J. LIANG *et al.*, *J. Mater. Sci. Lett.* **20** (2001) 795.
5. *Idem.*, *ibid.* **22** (2003) 811.
6. J. C. GROOTE *et al.*, *Phys. Rev. B* **50** (1994) 9798.
7. P. GALLO *et al.*, *ibid.* **47** (1993) 11830.
8. M. J. FRISCH *et al.*, "Gaussian 98, Revision A7" (Gaussian Inc., Pittsburgh, PA, 1998).

Received 23 February
and accepted 22 July 2005