Nuclear Magnetic Resonance Study of ^{23}Na Nucleus in NaBrO$_3$ Single Crystal

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The nuclear magnetic resonance of the ^{23}Na nucleus in a NaBrO$_3$ single crystal was investigated at the temperature range of 200 K~410 K. The tendencies of temperature dependence of the nuclear quadrupole coupling for the two magnetically inequivalent Na(I) and Na(II) centers are found to be opposite to each other. The nuclear spin-lattice relaxation mechanism of ^{23}Na in the NaBrO$_3$ crystal is investigated, and the result revealed that the Raman process is dominant in the temperature range investigated. The relaxation process of the ^{23}Na nuclear spins was well described by a single exponential function in time. The T_1 values of the ^{23}Na nuclei in the NaBrO$_3$ single crystal decreased with increasing temperature. The calculated activation energy for the ^{23}Na is 0.032 ± 0.002 eV.

Keywords : magnetic resonance, NaBrO$_3$ crystal, relaxation mechanism, activation energy

1. Introduction

Cubic NaBrO$_3$ crystal is well known to exhibit many interesting optical properties including optical rotation and electro-optic effects. Stimulated Raman scattering (SRS) in NaBrO$_3$ crystal to allow for the efficient generation of multiple Stokes and anti-Stokes emission was found by P. Franz et al. [1]. The BrO$_3^-$ groups occupy sites with a four-fold multiplicity and a symmetry of three. Compared to isomorphous and SRS-active NaClO$_3$, NaBrO$_3$ has been found to exhibit higher Vickers hardness and grinding hardness and a higher thermal stability. NaBrO$_3$ is a nonlinear material for applications such as Raman shifters or Raman lasers in the visible and near-IR range [1].

Frequency shifting of pico- and nano-second laser pulses is of interest for ecology monitoring techniques and for the generation of specific multiple wavelength cascades covering wide spectral regions in the infrared and visible ranges. This motivated the realization of an all-solid-state Raman laser at the base of NaBrO$_3$. With cubic NaBrO$_3$, J. Findeisen et al. [2] realized for the first time an all solid-state Raman laser using a simple set-up. NaBrO$_3$ crystal is a promising candidate for efficient Raman lasers in comparison to Ba(NO$_3$)$_2$, KGd(WO$_4$)$_2$, and PbWO$_4$ [2].

The NaBrO$_3$ crystal belongs to the cubic structure (acentric space group P2$_1$3) with the lattice constant 0.6555 nm [3]. The unit cell consists of four molecules (20 atoms). They form low trigonal pyramids. The structure is shown in Fig. 1. The bond between Na ion and BrO$_3$ ion is generally ionic [4]. The BrO$_3$ ion is a flat trigonal pyramid having oxygen atoms as its base. The binding between O-Br is largely a covalent structure. From the symmetry of the flat trigonal pyramid of oxygens, the symmetrical axes of the gradient of the electric field at the nuclear spins of Br are the lines passing through the Na and Br nuclei. Fig. 1 shows this axis of symmetry.

For the Na-Br distances in NaBrO$_3$, the ionic radius of Na ions is 0.095 nm and that of Br ion is 0.195 nm, while their sum is 0.290 nm which is shorter than the nearest distance of Na-Br of 0.342 nm. This means that the binding between Na and Br is partly covalent and the nuclear spin levels of Na has quadrupole splittings, while the symmetry axis of the field gradient at the Na nucleus is the same as that of Br [5].

Several nuclear quadrupole resonances of NaBrO$_3$ crystals [6-9] have been studied for many years. Nuclear magnetic resonance (NMR) is a good technique for the investigation of microscopic information on the materials. The spin-lattice relaxation rate of the nuclei in the host crystal reflects the dynamics of the crystal, such as the nucleus-phonon interaction, and indicates the ease at which the excited state energy of the nuclear system is transferred into the lattice. In this paper, we measured the

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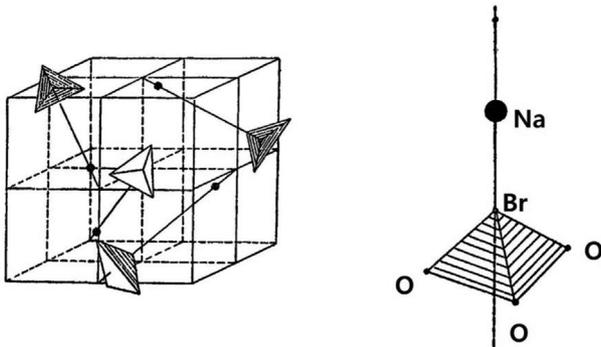
Fig. 1. Crystal structure of $NaBrO_3$ in the unit cell. The vertical line is the symmetric axis of the electric field gradient at the Na and Br sites.

NMR spectra and spin-lattice relaxation time of a ^{23}Na nucleus by using a pulse NMR spectrometer to obtain detailed information about the dynamics of a $NaBrO_3$ crystal. This paper documents these new investigations of NMR for the $NaBrO_3$ crystal.

2. Experiments

The spin-lattice relaxation times T_1 of the ^{23}Na in $NaBrO_3$ single crystals were measured using the Bruker 200 MHz FT NMR spectrometer at the Korea Basic Science Institute Seoul Western Center. The static magnetic field was 4.7 T and the central radio frequency was set to $\omega_o/2\pi=52.9015$ MHz for the ^{23}Na nucleus. The spin-lattice relaxation times were measured using the saturation recovery pulse sequence, sat-t–$\pi/2$-acq, for the ^{23}Na nucleus. The width of the $\pi/2$ pulse was 1.8 μs for the ^{23}Na nucleus. The temperature-dependent NMR measurements were obtained at the temperature range of 200-410 K. The samples were maintained at constant temperatures by controlling the nitrogen gas flow and heater current.

The ^{23}Na NMR spectrum in $NaBrO_3$ single crystal at room temperature is shown in Fig. 2 when the magnetic field B was applied along the crystallographic c-axis. This spectrum is obtained by Fourier transform of the free induction decay for the ^{23}Na NMR. Three resonance lines are expected because of the quadrupole interaction of the ^{23}Na (I=3/2, 100%) nuclei with the electric field gradient (EFG) under a strong magnetic field. However, six resonance lines are obtained in all temperature ranges when magnetic field B is parallel to the crystallographic c-axis. The line width of the central line for the ^{23}Na nucleus at room temperature is about 3 kHz. However, while the central transition remains constant, the interval between the central and satellite lines is found to change as the temperature increases.
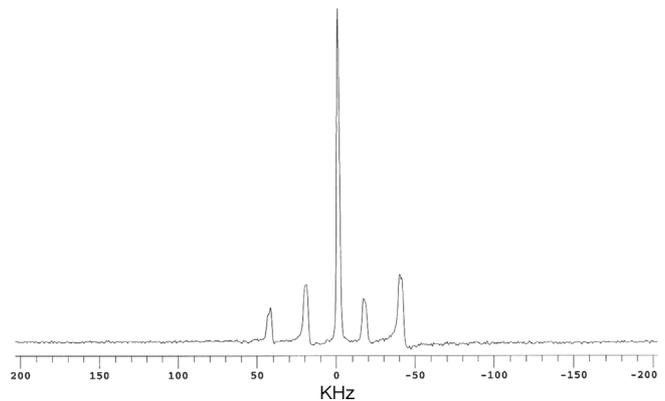

Fig. 2. Typical nuclear magnetic resonance spectrum of ^{23}Na nucleus at 300 K operating at $\omega_o/2\pi=52.9015$ MHz. The inner satellite line within ± 30 kHz is denoted as Na(I) center, whereas the outer side ± 30 kHz is denoted as Na(II) center.

3. Analysis and Discussion

Each unit cell has four Na ions. In the $NaBrO_3$ crystal, six NMR lines of Na nucleus were obtained at all temperature ranges investigated. One of the typical NMR spectra of ^{23}Na along the c-axis at room temperature is shown in Fig. 2. The four Na nuclei in the unit cell give two sets of NMR signals (six resonance signals) for the ^{23}Na nuclei in the $NaBrO_3$ crystal across the temperature range investigated. Two Na nuclei in the unit cell give a Na(I) NMR center and the other two Na nuclei in the unit cell give a Na(II) NMR center. The inner satellite lines within ± 30 kHz are denoted as a Na(I) center, whereas those outside ± 30 kHz are denoted as a Na(II) center. Two sets of NMR signals originated from the Na(I) and Na(II) centers. The central lines of the Na(I) and Na(II) centers merge into one resonance line. We found that two sets of NMR signals originated from the crystal symmetry, rather than from the twin structure of the $NaBrO_3$ crystal. The central transition ($|1/2>\leftrightarrow|-1/2>$) was not shifted by the quadrupole interaction, but the satellite transitions ($|3/2>\leftrightarrow|1/2>$) and ($|-1/2>\leftrightarrow|-3/2>$) were shifted. The line width for ^{23}Na at room temperature is about 3 kHz and slightly decreases with increasing temperature.

The nuclear quadrupole splitting of the Na(I) center is found to increase with increasing temperature, whereas that of the Na(II) center is found to decrease with increasing temperature. The trend of the Na(I) center is opposite that for the Na(II) center, as shown in Fig. 3. The temperature dependence of the quadrupole splitting is usually analyzed in terms of the Bayer theory, taking into account only the rigid-body vibration of the molecule [10-12]. The obtained temperature dependence of the quadrupole
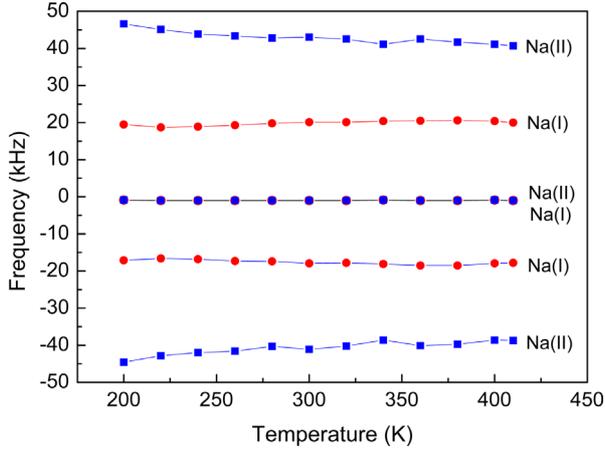
Fig. 3. (Color online) Zeeman splitting of NMR spectrum for ^{23}Na in NaBrO$_3$ single crystal. The zero point is 52.9015 MHz.

Fig. 4. (Color online) Magnetization recovery traces of ^{23}Na in NaBrO$_3$ crystal as a function of delay time at several different temperatures. The solid lines are fitted using Eq. (1).

coupling constant (QCC) of the Na(II) center can be explained with a single torsional mode for Na(II). However, the Bayer theory cannot explain the temperature dependence on QCC of the Na(I) center shown in Fig. 3, because the theory will always predict a decreasing coupling constant with increasing temperature since the amplitude of the rigid body vibration increases with temperature.
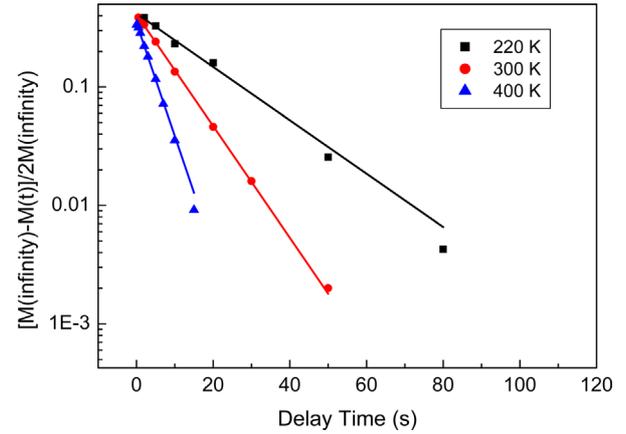
The spin-lattice relaxation times T_1 for ^{23}Na in NaBrO$_3$ single crystals were measured as a function of temperature. The saturation recovery traces of the magnetization were measured at a temperature range of 200-410 K for the ^{23}Na nucleus. The measured magnetization recoveries $[M(\infty) - M(t)]/2M(\infty)$ for the ^{23}Na (I=3/2) nucleus were found to satisfactorily fit a single exponential function with [13, 14].

$$[M(\infty) - M(t)]/2M(\infty) = \exp(-t/T_1), \qquad (1)$$

where $M(\infty)$ and $M(t)$ are the thermal equilibrium and time-dependent magnetizations, respectively, t is the time between the first and second pulses, and T_1 is the spin-lattice relaxation time.

The relaxation processes of the magnetic moment of the ^{23}Na nucleus as a function of delay time t are shown in Fig. 3 at temperatures of 220 K, 300 K, and 400 K. The relaxation of the ^{23}Na nuclear spins is found at a single exponential in time when all the resonance lines are uniformly excited. The T_1 values obtained by exciting only one line and by exciting all the lines are theoretically identical. Experimental data denoted by symbols fit well to Eq. (1) for each temperature.

The interaction of the nuclear quadrupole moment with the lattice vibration is a very important relaxation mechanism for the nuclear spin $I \geq 1$ in many crystals.

One of the major contributions to the spin-lattice relaxation for the nuclear spin $I \geq 1$ could be the quadrupolar interaction of the electric quadrupole moment of the nucleus with the lattice vibrations. The coupling can generally be written with a spin-lattice Hamiltonian [15]. At a temperature considerably below the melting point of the crystal, we can reasonably assume that the thermal stress should be small and only the first few terms are important. The first order term represents the absorption or emission of a single phonon (direct process). The next second order term indicates the emission or absorption of two phonons, or the absorption of one phonon followed by the emission of another phonon (Raman process). In the direct process, the spin-lattice relaxation rate $1/T_1$ is proportional to the square of the Larmor frequency for the nucleus, ω_0^2, and to the absolute temperature T. On the other hand, the Raman process provides a relaxation rate proportional to the square of the temperature at the high temperature limit [16, 17]. The Orbach process is another two-phonon process, but it provides an exponential behavior with temperature at the relaxation rate [15].

The temperature dependence of the nuclear spin-lattice relaxation rate $1/T_1$ for the ^{23}Na nucleus in the NaBrO$_3$ crystal was obtained and is shown in Fig. 5. The relaxation time of the ^{23}Na nuclei does not undergo any abrupt changes within the experimental temperature range of 200-410 K, which indicates that no phase transitions occur within this temperature range. The $1/T_1$ values of ^{23}Na were found to increase with an increase in the temperature. This is reasonable because the lattice vibration is more effective when the crystal temperature is increased, and the relaxation time is then shorter with increasing temperature.

The T_1 values for ^{23}Na in the NaBrO$_3$ crystal can be
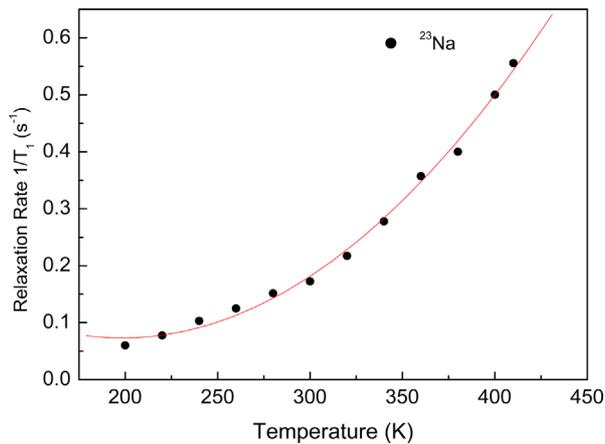
Fig. 5. (Color online) Temperature dependence of spin-lattice relaxation rate $1/T_1$ for ^{23}Na in NaBrO$_3$ crystal. The solid line is fitted by assuming Raman processes.

explained in terms of a relaxation mechanism in which lattice vibrations are coupled to the nuclear electric quadrupole moments. The relaxation rate is proportional to the square of the temperature for the nuclei in the investigated temperature range (solid line in Fig. 5). Therefore, the temperature dependence of the ^{23}Na relaxation rate in the NaBrO$_3$ crystal is in accordance with Raman processes. The Raman process is more effective than the direct process for nuclear quadrupole relaxation in our experiment. Namely, the dominant relaxation mechanism for the nuclei is the coupling of these moments to the thermal fluctuations of the local electric field gradients via the Raman spin-phonon process. Since our measurement was taken with a single crystal sample with no
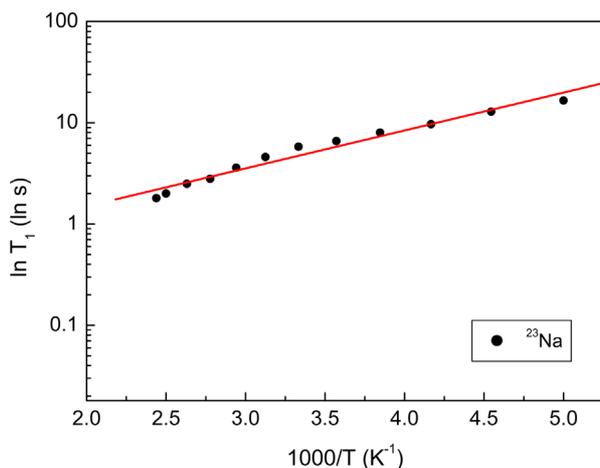
Fig. 6. (Color online) Semi log plot of spin-lattice relaxation time vs. the reciprocal temperature in the entire temperature region. The slope of the solid line represents the activation energy.

appreciable impurities, the present result represents a more reliable feature of the intrinsic behavior of the relaxation process in NaBrO$_3$.

The activation energy of the ^{23}Na nuclei in NaBrO$_3$ single crystals was determined using the equation $T_1 = A_o \exp(E_a/k_B T)$, where E_a and A_o are the activation energy and the pre-exponential factor, respectively, while k_B and T are the Boltzmann constant and the temperature, respectively. The plot of the natural logarithm of T_1 as a function of inverse temperature is hence linear, with a slope that is directly related to the activation energy. From the gradient of the graph in Fig. 6, we obtained the activation energy of 0.032 ± 0.002 eV, which is the energy required to activate the nucleus and to allow it to participate in the spin-lattice relaxation mechanism of the of ^{23}Na nucleus in the NaBrO$_3$ single crystal.

4. Conclusions

The NMR of the ^{23}Na nucleus in the NaBrO$_3$ single crystal was investigated by employing a FT-NMR spectrometer in the temperature range of 200 K-410 K. Two sets of ^{23}Na spectra are obtained when B//c-axis. These two sets of spectra are found to originate from the two magnetically inequivalent Na(I) and Na(II) sites in a NaBrO$_3$ single crystal. The nuclear quadrupole coupling constant of the Na(I) center actually increases with increasing temperature, whereas that of the Na(II) center decreases with increasing temperature. The tendencies of the temperature dependence of the nuclear quadrupole coupling for the two magnetically inequivalent Na(I) and Na(II) centers are found to be opposite each other. The line width of the central line for the ^{23}Na nucleus at room temperature is about 3 kHz.

From the ^{23}Na NMR study, the relaxation mechanism of ^{23}Na was investigated by determining the spin-lattice relaxation time, T_1, of the ^{23}Na in the NaBrO$_3$ crystal. The magnetization recoveries for the ^{23}Na nuclear spins were found to satisfactorily fit a single exponential function in time when all the resonance lines are uniformly excited. The spin-lattice relaxation time T_1 values of the ^{23}Na nuclei in the NaBrO$_3$ single crystal continuously decreased with increasing temperature. This means that phase transitions do not occur within the experimental temperature range. The dominant relaxation mechanism in the investigated temperature range can be inferred as the Raman process because the spin-lattice relaxation rate $1/T_1$ of the ^{23}Na nucleus in the NaBrO$_3$ crystal is proportional to the square of the temperature (T^2). Namely, the lattice vibrations are coupled to the nuclear electric quadrupole moments; the dominant relaxation mechanism

is the coupling of these moments to the thermal fluctuations of the local electric field gradients via the Raman spin-phonon process. The activation energy calculated for the ^{23}Na nucleus in the NaBrO$_3$ single crystal is 0.032 ± 0.002 eV.

References

[1] P. Franz, P. Egger, J. Hulliger, J. Findeisen, A. A. Kaminskii, and H. J. Eichler, Phys. Stat. Sol. (b) **210**, R7 (1998).

[2] J. Findeisen, J. Hulliger, A. A. Kaminskii, H. J. Eichler, R. Macdonald, P. Franz, and P. Peuser, Phys. Stat. Sol. (a) **172**, R5 (1999).

[3] R. W. G. Wyckoff, Crystal Structures, Inter-science Publishers, Inc., New York (1953).

[4] L. Pauling, The Nature of the Chemical Bond, Oxford Univ. Press, London (1952).

[5] K. Kano, J. Phys. Soc. Jan. **13**, 975 (1958).

[6] R. F. Tipsword, J. T. Allender, E. A. Stahl, and C. D. Williams, J. Chem. Phys. **49**, 2464 (1968).

[7] C. J. Whidden, C. D. Williams, and R. F. Tipsword, J. Chem. Phys. **50**, 507 (1969).

[8] D. D. Early, R. F. Tipsword, and C. D. Williams, J. Chem. Phys. **55**, 460 (1971).

[9] E. A. Stahl and R. F. Tipsword, Magn. Resonance in Chemistry **28**, 95 (1990).

[10] H. Bayer, Z. Physik **130**, 227 (1951).

[11] T. C. Wang, Phys. Rev. **99**, 566 (1955).

[12] T. P. Das and E. L. Han, Nuclear Quadrupole Resonance Spectroscopy, Academic Press, New York (1958) Chap. 1.

[13] W. W. Simmons, W. J. O'Sullivan, and W. A. Robinson, Phys. Rev. **127**, 1168 (1962).

[14] W. E. Blumberg, Phys. Rev. **119**, 79 (1960).

[15] A. Abragam, The Principles of Nuclear magnetism, Oxford Univ. Press, Oxford (1961) Chaps. I and IX.

[16] R. L. Mieher, Phys. Rev. **125**, 1537 (1962).

[17] J. Van Kranendonk, Theory of quadrupolar nuclear spin-lattice relaxation, Physica **20**, 781 (1954).