Raman scattering investigations in tetragonal tungsten-bronze compounds.
II. $Ba_2K_xNa_{1-x}Nb_5O_{15}$ mixed crystals

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Low-frequency optical modes of $Ba_2K_xNa_{1-x}Nb_5O_{15}$ ceramics and crystals have been investigated for $0 \leq x \leq 1$ in both ferroelastic and paraelastic phases. The ferroelastic transition occurs only for $x < 0.5$ and the Curie temperatures T_0 are determined as a function of x from the splitting of the E modes of the tetragonal phase into the B_1 and B_2 modes of the orthorhombic phase. These modes are then followed between T_0 and 1.5 K and comparisons are made with their already-known behavior in $Ba_2NaNb_5O_{15}$. The interest of Raman scattering as a tool of characterization of $Ba_2K_xNa_{1-x}Nb_5O_{15}$ crystals, where the actual composition differs from that of the starting melt, is pointed out.

I. INTRODUCTION

The present study is complementary to a previous one[1] which was devoted to phase transitions of $Ba_2NaNb_5O_{15}$ and related compounds by means of Raman scattering. The $Ba_2K_xNa_{1-x}Nb_5O_{15}$ compositions which are now investigated are solid solutions with the tungsten-bronze structure in the whole range $0 \leq x \leq 1$. If one considers the end members, i.e., $Ba_2NaNb_5O_{15}$ and $Ba_2KNb_5O_{15}$, one realizes that the former undergoes a ferroelastic transition from the tetragonal to the orthorhombic systems while the latter remains tetragonal at all temperatures. It has been established[2] that the critical temperature T_0 which is situated around 300 °C for $Ba_2NaNb_5O_{15}$, decreases with increasing values of x. For starting melts corresponding to $x > 0.7$, no transition was detected through the twin structure, even on cooling to approximately 77 K. Besides, composition differences between the crystal and the melt were noticed[2,3]: the pulled crystals always contain a higher sodium concentration than the starting melt. As $Ba_2K_xNa_{1-x}Nb_5O_{15}$ crystals, corresponding to high enough values of x are free of domain structure[4] at room temperature they were considered as better candidates[5] for applications in optical devices than $Ba_2NaNb_5O_{15}$.

The investigated $Ba_2K_xNa_{1-x}Nb_5O_{15}$ samples are single crystals grown from an appropriate melt or polycrystalline ceramics prepared in solid phase. One can expect that the materials prepared in the latter conditions have the composition defined by the starting products and do not suffer, as the pulled crystals, any potassium segregation phenomenon from the initial melt.

We restrict our Raman study to the low-frequency part of the spectra ($\omega < 180$ cm^{-1}). Several properties of the vibrational modes, found in the study of

$Ba_{2+x}Na_{1-2x}Nb_5O_{15}$ solid solutions[1] will be particularly investigated, like the splitting of the E modes of the quadratic phase into two components $B_1(x)$ and $B_2(y)$ below T_0 which leads to the determination of this critical temperature, and the presence as well as the softening of a characteristic mode of $B_2(y)$ symmetry, the intensity of which gives an estimate of the magnitude of the crystal orthorhombicity. Furthermore, its frequency is the lowest among the observed optical modes in these compositions.

II. EXPERIMENTAL RESULTS

We have performed a set of experiments on $Ba_2K_xNa_{1-x}Nb_5O_{15}$ ceramics for different values ($x = 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.8, 1$) of the concentration x. The different compositions were obtained by solid phase reactions, $BaCO_3$, K_2CO_3, Na_2CO_3, and Nb_2O_5 serving as starting materials. The method is described in Ref. 6. The sintering of the final product was performed in air at 50° below the appropriate predetermined[3] solidus temperature (~ 1350 °C) during 20 hours. Powder x-ray diffraction allowed the measurement of the lattice parameters vs x. The values of the $a (\simeq b)$ and c parameters at room temperature undergo variations with respect to the composition which can be expressed with a good approximation by the Vegard's law:

$$a(x) = 12.459 + 0.092x \ ,$$

$$c(x) = 3.990 + 0.033x \ ,$$

where the increment with x of both parameters is due to the increase of the alkaline earth cation radii ($r_{Na^+} = 0.95$ Å, $r_{K^+} = 1.33$ Å). Although the light scattered by ceramics is unpolarized, only the B modes of the orthorhombic phase (or the E mode of

the quadratic phase) which are much more intense[1] than the modes of other symmetries, appear below 180 cm^{-1}.

When x varies from 0 to 1, the Raman spectra of ceramics are rather similar, except a progressive frequency shift towards the Rayleigh line. The relative intensities of the Raman lines also show some variations from one spectrum to another. Besides, no broadening of the different line occurs and no increase of the background level has been observed in the whole range of x, which might be assigned to a disorder effect. The spectra obtained from ceramics are used to determine the actual composition of the crystals. Among the Raman lines, the most intense and the best defined one helps in their calibration. Its frequency ω^* varies from 45 to 37 cm^{-1} for $0 < x < 1$.

The investigated single crystals are of good enough optical quality to perform polarized Raman studies. They are grown by the Czochralski method in platinum crucibles using a high-frequency 20-kW generator. A series of compositions were prepared by melting carefully mixed commercial high-grade niobium pentoxide and barium, sodium, and potassium carbonates.

We have already pointed out the difference between the compositions of the pulled crystals and the starting melt. Actually, a better approach of the investigated mixed crystals is given by the formula $Ba_{2+y}(K_xNa_{1-x})_{1-2y}Nb_5O_{15}$. In Table I, columns 2 and 3, are given the values of x and y corresponding to X which is the mole% $Ba_2KNb_5O_{15}$ in the starting melt. They have been obtained by radiochemical analysis. One can notice that the values of y are not important and vary in a relatively small range (between 0.1 and 0.15) and are very comparable with those determined in Ref. 3. Thus, one can, to a good approximation, neglect the influence of y in the lattice dynamics of these compounds, and consider $Ba_2K_xNa_{1-x}Nb_5O_{15}$ as the formula associated to these compounds.

We have investigated at room temperature the spectra corresponding to the four crystals of Table I. The value of ω^* measured on these spectra [ω^* in single crystals is taken in the orthorhombic phase as the mean value of two very close $B_1(x)$ and $B_2(y)$ modes] compared to the results on ceramics, allows a Raman scattering determination of x. Comparison between column 2 and 4 shows that the results obtained for the concentration x by means of the Raman technique are in good agreement with those determined by radiochemical methods. The precision obtained by light scattering is poor for weak values of x, but becomes interesting for $x > 0.2$.

As in $Ba_2NaNb_5O_{15}$ (Ref. 1), a determination of the transition temperature T_0 is obtained by means of Raman scattering since the $B_2(y)$ and $B_1(x)$ spectra, observed versus temperature through $z(yz)x$ and $z(xz)y$ scattering configurations for instance, merge precisely at T_0. The transition temperatures of the different crystals as obtained from our observations are plotted in Fig. 1 versus the concentration x. For $x > 0.5$, no transition was detected. Our results agree with those of O'Kane et al.,[3] which are reported on the same diagram. In Ref. 3 the values of T_0 were obtained through the detwinning of polydomain samples. The two methods (Raman scattering and domain-structure observations) thus give the same results. For $0 \leqslant x < 0.5$, the T_0 variations are given by the formula $T_0 = 570(1 - 0.89x)$ K.

As an example, the $B_1(x)$ and $B_2(y)$ are shown in Fig. 2 for $x = 0.33$. When the temperature is increased, the spectra which are different at room temperature end by merging completely at a temperature $T_0 = 390 \pm 10$ K. We have also reported (Fig. 3) the low temperature $B_2(y)$ spectra for $x = 0.33$. Around $T = 200$ K the characteristic mode begins to be noticeable and its frequency ω can be measured versus temperature. It can also be noticed that the nearest line, of frequency ω^*, undergoes the same, though less important in amplitude, kind of softening. We have plotted on Fig. 4, the square frequency ω^2 of

TABLE I. Compared results of the radiochemical analysis and the Raman measurements of the effective composition of $Ba_{2+y}(K_xNa_{1-x})_{1-2y}Nb_5O_{15}$ crystals.

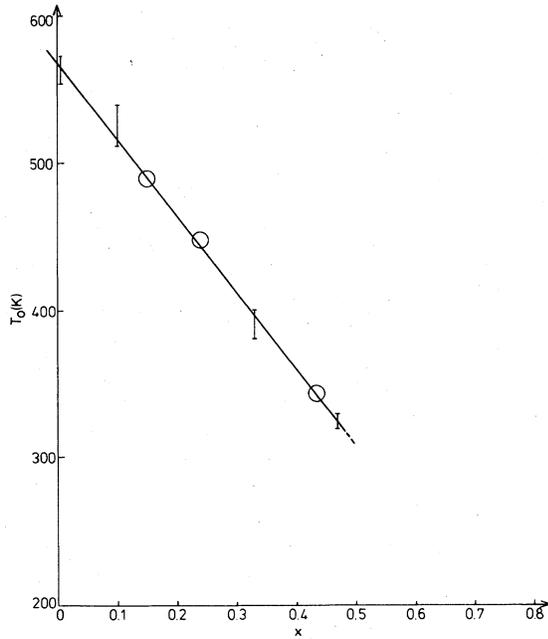| Mole% $Ba_2KNb_5O_{15}$ in the melt	x values in the crystal (radiochemical analysis)	y values in the crystal (radiochemical analysis)	Raman determination of x (from comparisons with ceramics)
$X_1 = 20$	0.095 ± 0.003	0.100 ± 0.003	0.075 ± 0.075
$X_2 = 60$	0.330 ± 0.003	0.144 ± 0.004	0.325 ± 0.025
$X_3 = 70$	0.47 ± 0.01	0.130 ± 0.015	0.500 ± 0.02
$X_4 = 80$	0.62 ± 0.01	0.150 ± 0.015	0.640 ± 0.02

FIG. 1. Transition temperature T_0 vs concentration x as obtained from Raman spectra. The circles represent Ref. 3 measurements.
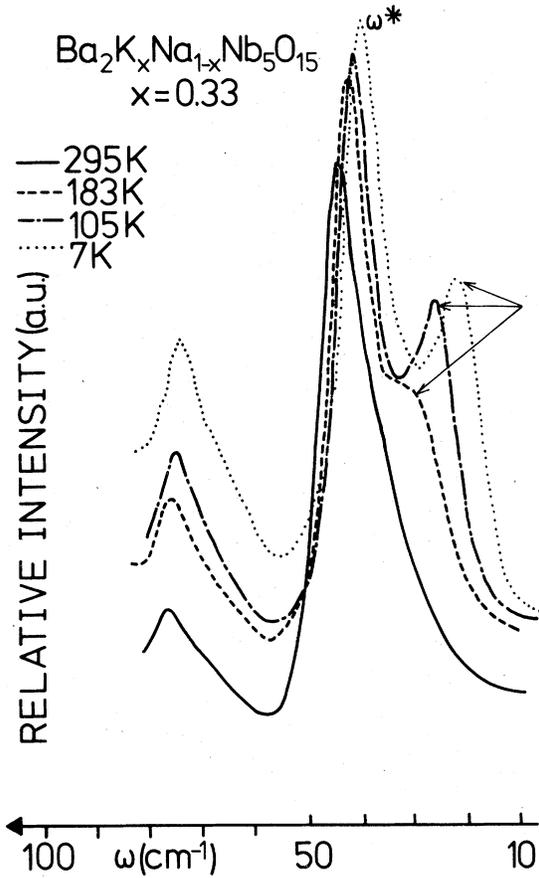
FIG. 2. $B_1(x)$ and $B_2(y)$ modes in $Ba_2K_{0.33}Na_{0.67}Nb_5O_{15}$ observed, respectively, in $z\,(xz)y$ and $z\,(yz)x$ scattering geometries. Above $T_0 \simeq 390$ K, the spectra which are represented on the same scale, merge to a single E mode.

FIG. 3. $B_2(y)$ modes in $Ba_2K_{0.33}Na_{0.67}Nb_5O_{15}$ vs temperature. From 200 to 1.5 K, the characteristic mode (indicated by an arrow) is very clear and its softening can be easily followed. The next line of frequency ω^*, undergoes a smaller shift.
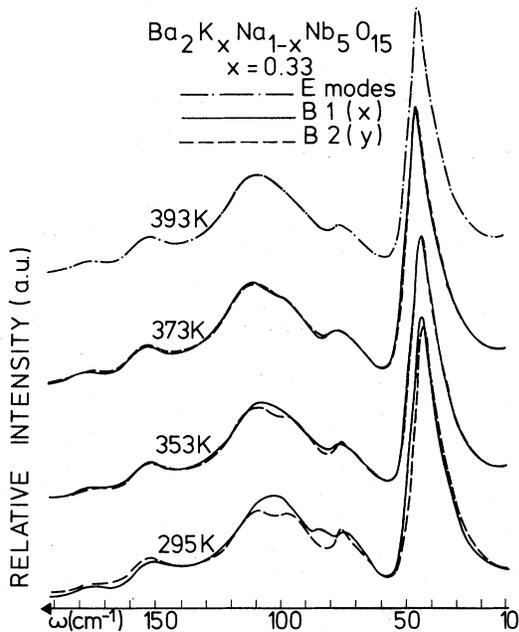
the characteristic mode, which varies linearly with temperature with the same slope $A = 2 \pm 0.1$ cm^{-2}/K as in $Ba_2NaNb_5O_{15}$.

In the case of $Ba_{2+x}Na_{1-2x}Nb_5O_{15}$ it has been observed[1] that the intensity of the characteristic mode reaches a maximum for $T = T_m$, and then decreases again on cooling below T_m. This behavior was then interpreted as connected to the degree of orthorhombicity, which undergoes an enhancement, followed by a decrease (i.e., a tendency to a return to the quadratic phase). Such a tendency has not been observed in our $Ba_2K_xNa_{1-x}Nb_5O_{15}$ crystals since the intensity of the characteristic mode increases constantly on cooling from T_0 to 1.5 K. Thus, the introduction of potassium atoms in place of sodium, for values of x as small as $x = 0.1$, cancels this peculiar low-temperature behavior in $Ba_{2+x}Na_{1-2x}Nb_5O_{15}$ crystals. Steric considerations on alkaline-earth cations are probably to be put forward to explain the observed difference.
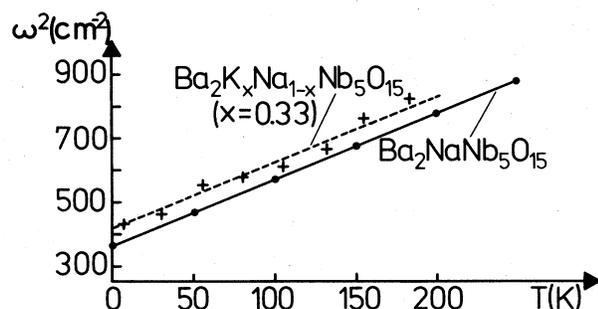
FIG. 4. Square frequency ω^2 of the characteristic mode in $Ba_2K_{0.33}Na_{0.67}Nb_5O_{15}$ and $Ba_2NaNb_5O_{15}$ vs temperature. The variations are represented by two parallel lines.

Two additional remarks can be made concerning the general features of the Raman modes. The first one is that the $Ba_2K_xNa_{1-x}Nb_5O_{15}$ solid solutions, considered as mixed crystals[7] in the range $0 < x < 1$ are such that almost all their optical modes belong to the one-mode type. Yet, we have observed that the mode situated at 76 cm^{-1} in $Ba_2NaNb_5O_{15}$ (62 cm^{-1} in $Ba_2KNb_5O_{15}$) displays a two-mode behavior. Details of the variations of the frequency of the Raman lines vs x are given elsewhere.[8] The second one is even though the E modes of the tetragonal phase do not vary with temperature, they give rise below T_0 to B modes which are strongly temperature dependent. We have noticed that for all x values, the different B

modes have their intensity related to the difference between the crystal temperature and its critical temperature T_0. For example, samples with different compositions, observed 100 K below their transition temperature show spectra which differ only by a frequency shift.

III. CONCLUSION

We have studied the main vibrational-mode features of $Ba_2K_xNa_{1-x}Nb_5O_{15}$ mixed crystals in the whole range of x values in the paraelastic phase as well as in the ferroelastic phase. The values of the Curie temperature determined by Raman scattering coincide with those obtained from the twin disappearance. Besides, the atomic segregation which occurs during the crystal growth, does not seem to affect the $Ba_2K_xNa_{1-x}Nb_5O_{15}$ ceramics prepared in solid phase. On the other hand, the vibrational frequencies obtained on ceramics allow a quick concentration determination of pulled crystals of unknown composition, by simple comparisons of the Raman spectra.

The lowest-frequency mode, characteristic of the orthorhombic phase is seen for $0 \leq x < 0.5$. It undergoes a softening when the temperature is lowered from T_0 to 1.5 K. Besides, introduction of small quantities of K atoms in replacement of Na cancels the tendency to a return to the quadratic phase observed when cooling the $Ba_{2+x}Na_{1-2x}Nb_5O_{15}$ crystals.

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