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FULL PAPER

Structural Determination of Atomic Substitution Ratio in $(K_{1-x}Rb_x)_2SeO_4$ Mixed Crystal System

Shinsuke SAWAE, Terumi NAKASHIMA¹, Hirotake SHIGEMATSU²,
Hironobu KASANO and Hiroyuki MASHIYAMA *

Faculty of Science, Yamaguchi University, Yamaguchi 753-8512,

¹*Center for Instrumental Analysis, Yamaguchi University, Yamaguchi 753-8512,*

²*Faculty of Education, Shimane University, Matsue 690-8504*

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In order to explain why Rb_2SeO_4 remains in normal phase down to 0 K while K_2SeO_4 transforms into the modulated phase at finite temperature, crystal structures of the mixed system have been refined at room temperature by X-ray single crystal analysis. Rb ion can be substituted for K ion with keeping the macroscopic symmetry of space group $Pnam$. Larger size of Rb ion occupies preferentially site 1, while smaller K ion prefers site 2. Here the atomic distance between an alkali ion and oxygen atoms is longer at site 1 than at site 2. The mean substitution ratio coincides with that from chemical analysis, however, the crystallographic structure analysis is only one method to determine the ratios at each site separately. A sublattice model is discussed to interpret the ion replacing effect on the phonon dispersion relation of the mixed crystal system. The hardening of the soft mode branch can be predicted by the change of interactions between the SeO_4 tetrahedrons if the alkali ions are replaced.

KEYWORDS: potassium selenate, rubidium selenate, mixed crystal, substitution ratio, structure analysis, phase transition, sublattice model, soft phonon dispersion

1. Introduction

A crystal system of A_2BX_4 is one of the fully investigated compounds, because of existence of an incommensurate phase.¹⁾ Here A stands for either alkali ion such as Li, K or Rb, or NH_4 or $N(CH_3)_4$; B stands for divalent metallic ions, and X stands for halogen ions as F, Cl, Br or I; sometimes BX_4 represents SO_4 or SeO_4 . At room or higher temperature, many of the crystals take an orthorhombic β - K_2SO_4 -type structure with the space group $Pnam$: normal phase. It is a pseudo-hexagonal structure, and transforms to the incommensurately modulated one at a transition temperature T_i , which is usually followed by the commensurate phase with further lowering temperature.

Among many such crystals, K_2SeO_4 has been most extensively investigated. A well defined soft phonon mode has been recognized by neutron scattering study.²⁾ Other isomorphic

*E-mail: mashi@sci.yamaguchi-u.ac.jp

crystals, Rb_2ZnBr_4 , Rb_2ZnCl_4 and their family have been also investigated to elucidate the transition mechanism. But the soft modes were overdamped in Rb_2ZnBr_4 and others around T_i .³⁾ It has been widely believed that the soft phonon mode is underdamped only in K_2SeO_4 .

Although the crystal structure of Rb_2SeO_4 ⁴⁾ is isomorphous to K_2SeO_4 ,⁵⁾ the Rb compound remains in the normal phase down to 0 K. On the other hand, computer simulations have predicted that the phonon branch of Rb_2SeO_4 may become unstable at -6 K.⁶⁾ Depression of the phonon branch has been observed really by means of neutron inelastic scattering.⁷⁾ The dispersion takes minimum at the zone boundary in the extended zone scheme, and the minimum frequency decreases with lowering temperature. This suggests that a virtual transition may take place at negative temperature.

It is empirically recognized that the ratio of A ion size to BX_4 tetrahedron size is related to the transition temperature and the transition sequence of the A_2BX_4 -type crystals.⁸⁾ To verify this size effect, a $(\text{K}_{1-x}\text{Rb}_x)_2\text{SeO}_4$ mixed crystal system has been investigated by substituting larger Rb ion for smaller K ion in K_2SeO_4 . If a small amount of K is replaced by Rb, then the normal to incommensurate transition temperature T_i decreases a little. When the substitution ratio x exceeds 0.3, the transition does not take place any more, though the phonon branch shows a tendency of softening around a wave number of $q = 1/3 - \delta$ (δ is a small misfit parameter). With further increasing x , the minimum point of the branch shifts toward the Γ point.⁹⁾

There are two different sites for K ion in the orthorhombic structure of K_2SeO_4 .⁵⁾ K ions at site 1 and SeO_4 tetrahedrons construct pseudo-hexagonal networks within the $b - c$ layer. On the other hand, K ions at site 2 connect SeO_4 tetrahedrons along the a -axis, the modulation wave number direction of the incommensurate phase. At site 1, K is surrounded by 11 oxygen atoms of SeO_4 tetrahedrons. The mean distance between K and O is 3.14 Å, which is about 0.2 Å longer than the mean distance between K at site 2 and O. K is surrounded by 9 oxygen atoms at site 2. It is considered that Rb ions can occupy site 1 easier than site 2 because of the difference of the K-O distance.

Many one-dimensional models have been proposed to explain the dispersion relation of K_2SeO_4 .¹⁰⁾ The effective interactions between layered variables are introduced in some models.^{11,12)} In order to apply such models to the $(\text{K}_{1-x}\text{Rb}_x)_2\text{SeO}_4$ mixed crystal system, it should be clarified whether the substitution takes place randomly or selectively. Since a chemical analysis determines the total content of K and Rb, information about the replacement at each site can be obtained separately only by structure analysis.

X-ray diffraction intensities have been analyzed by least-squares method of the structure analysis. Since correlation among parameters was serious, constrained conditions were imposed on the calculation. Maximum entropy method has been also applied to check whether the result is free from constrains. It has been found that smaller K ion at site 1 is more easily replaced

Table I. The experimental condition and the summary of analysis in X-ray diffraction study for $(K_{1-x}Rb_x)_2SeO_4$ mixed crystal system. Here x is the mean substitution ratio, r is the sample radius, RD means the number of reflection data, R is the residual factor of the least-squares calculation, and x_1 and x_2 are the substitution ratios at site 1 and 2.

| sample | x | r (mm) | system | $2\theta_{max}$ ($^\circ$) | RD | R (%) | x_1 | x_2 |
|---------|------|----------|--------|------------------------------|------|---------|-------|-------|
| Rb 0% | 0 | 0.15 | AFC5R | 60 | 681 | 4.617 | 0 | 0 |
| Rb 10% | 0.06 | 0.245 | AFC5R | 65 | 859 | 2.766 | 0.05 | 0.01 |
| Rb 20% | 0.13 | 0.125 | MXC | 70 | 1035 | 2.486 | 0.12 | 0.01 |
| Rb 30% | 0.28 | 0.125 | AFC5R | 70 | 974 | 2.763 | 0.24 | 0.04 |
| Rb 40% | 0.36 | 0.15 | AFC5R | 65 | 811 | 3.628 | 0.27 | 0.09 |
| Rb 50% | 0.48 | 0.145 | MXC | 65 | 835 | 3.320 | 0.37 | 0.11 |
| Rb 60% | 0.51 | 0.105 | AFC5R | 60 | 643 | 4.607 | 0.38 | 0.13 |
| Rb 70% | 0.66 | 0.105 | MXC | 60 | 696 | 2.524 | 0.44 | 0.22 |
| Rb 80% | 0.80 | 0.105 | MXC | 65 | 843 | 2.789 | 0.48 | 0.32 |
| Rb 90% | 0.90 | 0.105 | MXC | 65 | 885 | 3.735 | 0.48 | 0.42 |
| Rb 100% | 1 | 0.15 | AFC5R | 70 | 972 | 5.897 | 1/2 | 1/2 |

by larger Rb ion. But the substitution takes place randomly with different weight at each site while keeping the mean space group to be $Pnam$.

2. Experimental

Single crystals were grown from aqueous solution containing K and Rb with molar ratio of $1-x$ and x . Transparent and colorless crystals were grown for nine sets: 10, 20, ... and 90 % content of Rb in aqueous solution. Crystals have been devoted to calorimetric measurement to determine the transition temperatures and to neutron scattering experiments to observe the phonon branch.⁹⁾

A small piece of crystal was cut and polished into a small sphere, and was mounted on a four-circle diffractometer at Center for Instrumental Analysis of Yamaguchi University. X-ray, Mo $K\alpha$ ($\lambda = 0.71068 \text{ \AA}$), from rotating anode was monochromated by graphite. Diffraction intensity was collected at room temperature by AFC5R(RIGAKU) system or MXC(MAC-HUBER) system. Absorption correction was applied for each spherical sample.

The space group was confirmed as $Pnam$ ($Z = 4$). Sample radius, measuring system, measured range of $2\theta_{max}$ and number of independent reflections are summarized in Table I. Pure K_2SeO_4 (Rb 0 %) and Rb_2SeO_4 (Rb 100 %) were also measured to compare with the mixed crystals.

Lattice parameters depend almost linearly on the substitution ratio x as shown in Fig. 1, which is in according to the Vegard's rule. The crystal structure parameters were refined

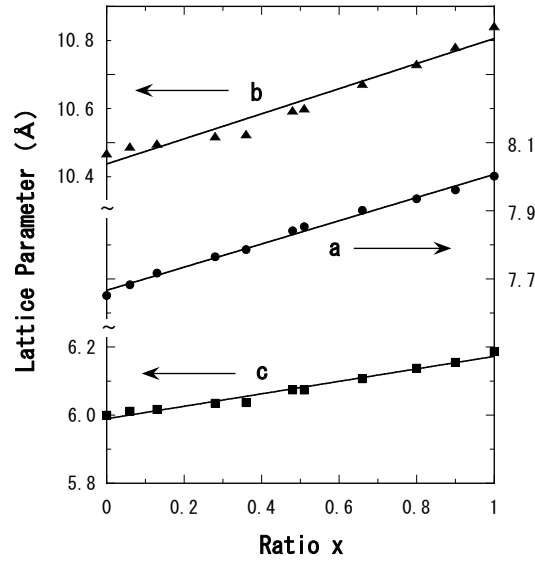


Fig. 1. Lattice parameters a , b , and c of $(K_{1-x}Rb_x)_2SeO_4$ mixed crystal system. The abscissa axis is the mean substitution ratio determined from the X-ray structural analysis.

by using the least-squares program system (AXS89).¹³⁾ Anisotropic thermal parameters were assumed for all atoms.

The maximum entropy method (MEM) for the structure analysis was also employed; the program system SMEED developed by Prof. Sakata and his coworkers¹⁴⁾ was modified to run on a personal computer. As for the diffraction data for MEM, the reflection intensity was scaled after the least-squares calculation by AXS89. The unit cell was divided into $36 \times 50 \times 28 = 50,400$ pixels, each pixel is almost cubic with $8 \times 10^{-3} \text{ \AA}^3$ volume. The charge density at the pixels was deduced by MEM calculations with the given total electrons in a unit cell.

3. Least-Squares Calculations

Although crystals were grown from a given molar ratio, the substitution ratio was also chosen as a fitting parameter in the least-squares calculation. Since the substitution ratios at site 1 and 2 may differ from each other, two variables x_1 and x_2 are introduced to represent two sites by a chemical formula $(K(1)_{1/2-x_1}Rb(1)_{x_1}K(2)_{1/2-x_2}Rb(2)_{x_2})_2SeO_4$. Here (1) and (2) represent the site 1 and 2, respectively. The mean substitution ratio is $x = x_1 + x_2$.

Moreover, K and Rb that sit on a same site may have different positional and thermal parameters; they are considered as independent variables throughout the calculation. Then it was found that thermal parameters and substitution ratios correlated with each other: the convergence of the calculation was too slow. So we fixed x_1 and x_2 , and refined positional and thermal parameters to get the residual parameter

$$R = \frac{\sum |F_{\text{cal}} - F_{\text{obs}}|}{\sum |F_{\text{obs}}|}. \quad (1)$$

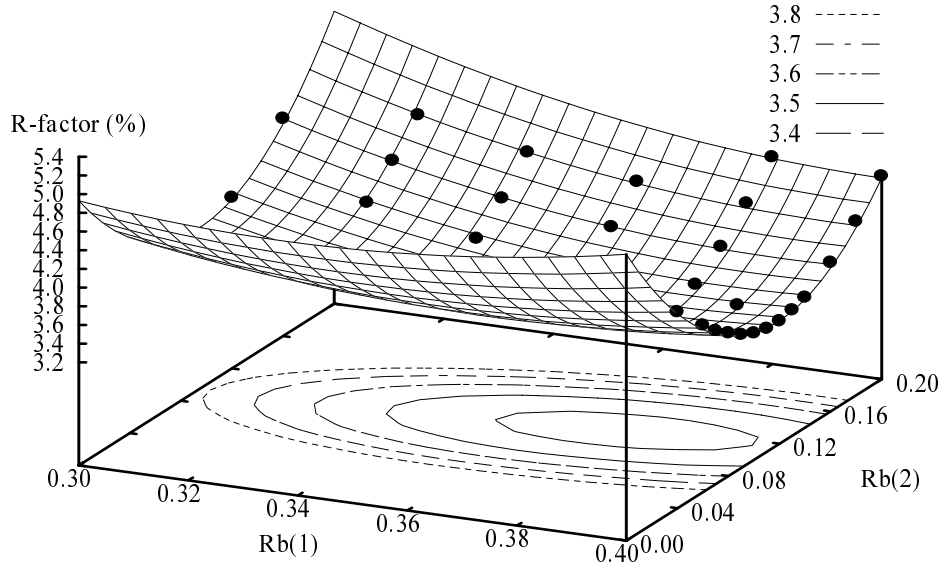


Fig. 2. Residual R surface as a function of substitution ratios x_1 and x_2 . The contour map is drawn on the $x_1 - x_2$ plane.

The obtained R can be plotted in a parameter space (x_1, x_2) as shown in Fig. 2, which is drawn for Rb 50 % crystal. The concave curve of the R surface has a minimum at $x_1 = 0.37$ and $x_2 = 0.11$, for which parameters the least-squares calculation was refined by using 835 reflections to give $R = 3.320$ % ($R_w = 4.046$ %, $S = 1.791$). At the final stage of calculations, two intense reflections of (002) and (031) were neglected because they were affected by secondary extinction. The final parameters are given in Table II.

The estimated substitution ratio is $x = 0.48$, almost in coincidence with the prepared ratio 50 %. K at site 1 can be replaced by Rb more easily than at site 2. The replacement ratio of site 1 is 74 % and that of site 2 is 22 %. The mean substitution ratio is 48 % in agreement with the chemical analysis (46.5 % by ICP method),⁹⁾ however, X-ray structure analysis can determine the ratio at each site separately.

Other crystals for 10 to 90 % were analyzed in the same manner. The results are summarized in Table I. The minimum R factor is $2.524 \sim 4.607$ %, which indicates that the least-squares calculations are satisfactory. The obtained substitution ratio at each site is plotted against the mean substitution ratio x in Fig. 3. The solid and dashed curves are obtained by fitting to a relation $x_j = (\frac{1}{2} + p_1(x-1) + p_2(x-1)^2)x$. The parameters are $p_1 = -0.497$ and $p_2 = -0.037$ for Rb(1). The total substitution ratio is compared with the result of chemical analysis (ICP) in Fig. 4. Generally the substitution ratio is smaller than the nominal value.

Table II. Structure parameters and substitution ratios for 50 % Rb content crystal. The occupation parameters for K and Rb represent $1/2 - x_1$ (or $1/2 - x_2$) and x_1 (or x_2), respectively. The estimated standard deviation is given in parentheses.

| atom | x | y | z | $U_{\text{eq}} (\text{\AA}^2)$ | x (or $1/2 - x$) |
|-------|------------|------------|-----------|--------------------------------|---------------------|
| Rb(1) | 0.1696(1) | 0.0879(1) | 1/4 | 0.0201(2) | 0.370(1) |
| Rb(2) | 0.9932(4) | 0.7082(3) | 1/4 | 0.0212(7) | 0.110(1) |
| K(1) | 0.1683(8) | 0.0877(6) | 1/4 | 0.0273(17) | 0.130(4) |
| K(2) | 0.9930(3) | 0.7079(2) | 1/4 | 0.0211(3) | 0.390(2) |
| Se | 0.22559(8) | 0.42020(6) | 1/4 | 0.0140(1) | |
| O(1) | 0.0180(8) | 0.4216(9) | 1/4 | 0.0570(29) | |
| O(2) | 0.3018(8) | 0.5642(6) | 1/4 | 0.0307(16) | |
| O(3) | 0.2963(7) | 0.3478(8) | 0.0319(8) | 0.0357(12) | |

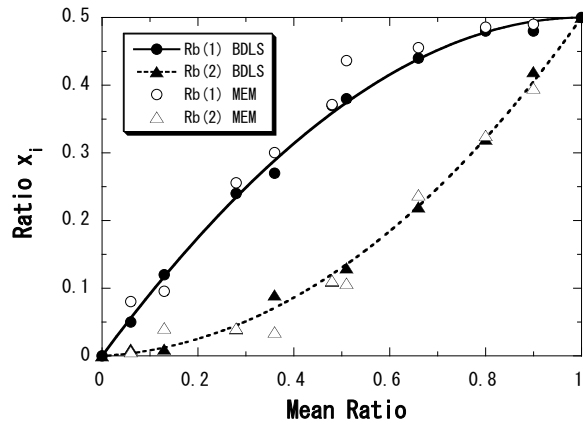


Fig. 3. Substitution ratio for Rb at two sites of K_2SeO_4 . Solid and open symbols represent least-squares calculation(BDLs) and MEM calculation, respectively. The abscissa axis is the mean substitution ratio. The solid and dashed curves are fitted relations for BDLs results.

The site 1 can be occupied by Rb more easily than the site 2. In the Rb rich side, the substitution is almost in agreement to the molar ratio in the solution. The substitution takes place randomly within each site. The space group reflecting the mean structure is $Pnam$ in the whole range of the substitution ratio.

The weak selection tendency that Rb can occupy site 1 easily than site 2 relates to the radius of the alkali atom: Rb is about 0.156 \AA larger than K in metallic state. The distance between the alkali ion and oxygen of SeO_4 is plotted in Fig. 5 after our structure analysis. In pure K_2SeO_4 , K(1) is surrounded by 11 oxygen atoms and K(2) by 9 ones.⁵⁾ The mean distance of the K-O distance is 3.134 \AA at site 1 and 2.928 \AA at site 2; the former is larger

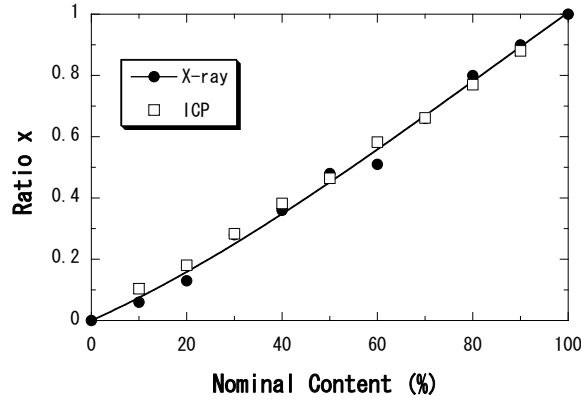


Fig. 4. Total substitution ratio for Rb in $(K_{1-x}Rb_x)_2SeO_4$ mixed crystal system. The X-ray result is compared to the chemical analysis(ICP). The abscissa axis is the Rb content in aqueous solution. The solid line shows the fitted relation for the X-ray analysis.

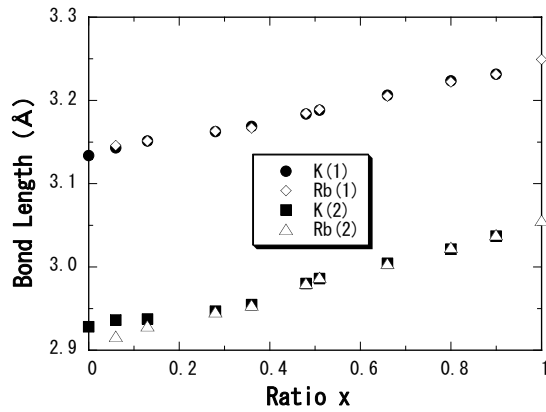


Fig. 5. The alkali to oxygen distance in $(K_{1-x}Rb_x)_2SeO_4$ mixed crystal system. The abscissa axis is the mean substitution ratio.

than the latter by 0.206 \AA . In pure Rb_2SeO_4 , Rb-O distance for site 1 is larger than that of site 2 by 0.193 \AA . The chemical features of the alkali ions resemble with each other, therefore Rb can occupy the larger K(1) site easily. With increasing Rb content in Fig. 5, both distances at site 1 and site 2 enlarge in the same manner. According to Shannon,¹⁵⁾ the ionic radius is 1.58 and 1.66 \AA for K^+ and Rb^+ , respectively. Since the atomic radius of O is 1.0 \AA , the alkali ions are not in touch with oxygen, and connect to SeO_4 with ionic bonding. This picture is supported by MEM analysis described in the following section.

4. Maximum Entropy Method

The observed structure factors scaled after the least-squares calculation were devoted to MEM calculations. The total electrons in the unit cell were fixed to the estimated value from the least-squares method. For each substitution ratio crystal, the MEM calculation converged at $R = 0.55 \sim 2.13$ %, where R is defined by eq. (1).

Since alkali ions are well separated from others, the charge number for each alkali ion is estimated by integrating the charge density around the each site. With assuming that K^+ and Rb^+ have 18 and 36 electrons, respectively, the substitution ratio x_j at site j is related to the electron charge Q_j by the relation

$$Q_j = 18 \times (1 - 2x_j) + 36 \times 2x_j, \quad (2)$$

at each site. The result is summarized also in Fig. 3; it is consistent with the least-squares calculation. It should be noted that there was neither direct constraint between x_1 and x_2 , nor assumption of substitution manner in the process of MEM calculation. Only the total charge number in a unit cell was given a priori. The consistency suggests that the assumption imposed in the least-squares calculation is appropriate.

5. Summary and Discussions

If some of K in K_2SeO_4 are replaced by Rb, the normal-to-incommensurate transition temperature T_i decreases. The crystal remains in the normal phase down to 0 K, if the substitution ratio exceeds 30 %.⁹⁾ A chemical analysis can determine only the mean substitution ratio, and cannot display where the substituted atom exists in the unit cell. In order to decide the site substitution ratio, X-ray crystal analysis has been done as described in the preceding sections.

As shown in Fig. 4, X-ray analysis gives almost the same mean substitution ratio with the chemical analysis. The substitution ratio of Rb ion in the crystal is almost the same that of the aqueous solution from which the single crystal is grown, though the mean ratio is a little small at K rich side. When the substitution ratio is less than 20 %, K at site 1 is mainly replaced by Rb, and Rb is rarely substituted into site 2 as shown in Fig. 3. On the other hand, site 1 is almost fully occupied by Rb at the Rb-rich end in the $(\text{K}_{1-x}\text{Rb}_x)_2\text{SeO}_4$ mixed crystal system.

Here we note again that three alkali ions at site 1 construct a hexagonal network with three SeO_4 tetrahedrons. On the other hand, alkali ions at site 2 connect the networks piling up along the a -axis. The mean distance between an alkali ion and oxygen is longer at site 1 than at site 2 by about 7 %. Therefore larger Rb ions prefer site 1.

Now let's discuss about the substitution effect on the transition temperature T_i , below which atoms incommensurately displace with a wave number along the a -axis. Iizumi *et al.* demonstrated that the observed dispersion relation for the soft phonon branch can be rep-

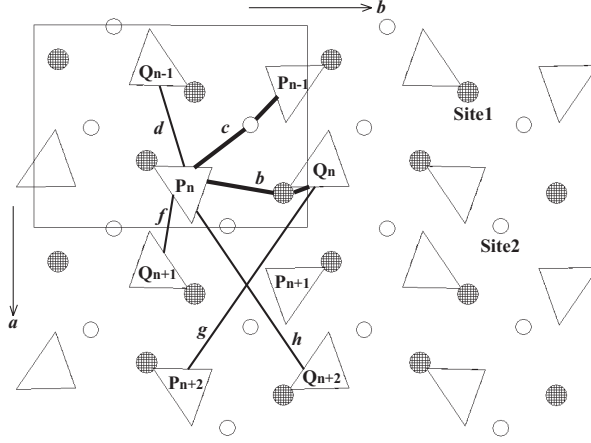


Fig. 6. Structure projected on the $a - b$ plane of the A_2BX_4 -type crystal. A unit cell is shown by a rectangle. Hatched and open circles are A atoms at site 1 and 2, respectively. Interactions between BX_4 tetrahedrons (triangles) are shown by bold lines with symbols of the interaction parameters.

represented by long range interactions between the layers separated from each other by a half cell-dimension along the a -axis.²⁾ Later, many models have been proposed to explain the incommensurate transition in A_2BX_4 -type crystals. Chen and Walker considered two independent modes and the couplings explicitly, and were successful to express a realistic phase diagram with a set of phenomenological parameters.¹¹⁾

Recently Ishibashi and Janssen proposed a sublattice model.¹²⁾ They introduced two variables P_n and Q_n , which describe the motion of two molecules related by n -glide symmetry in the layered network (see Fig. 6). These variables are coupled with a constant b within the network. Other parameters c and d represent coupling between layers. The potential energy for n -th layer is given by

$$U_n = \frac{b}{2}(P_n - Q_n)^2 + \frac{d}{2}(Q_n - P_{n+1})^2 + \frac{c}{2}((P_n - P_{n+1})^2 + (Q_n - Q_{n+1})^2). \quad (3)$$

Here we further introduce second and third nearest neighbor interactions as¹⁶⁾

$$U'_n = \frac{f}{2}(P_n - Q_{n+1})^2 + \frac{g}{2}(Q_n - P_{n+2})^2 + \frac{h}{2}(P_n - Q_{n+2})^2 + \frac{j}{2}((P_n - P_{n+2})^2 + (Q_n - Q_{n+2})^2) + \frac{k}{2}((P_n - P_{n+3})^2 + (Q_n - Q_{n+3})^2). \quad (4)$$

The soft phonon dispersion is represented by the following relation:

$$\omega(q) = [b + d + f + g + h + 2c(1 - \cos \frac{q}{2}) + 2j(1 - \cos q) + 2k(1 - \cos \frac{3q}{2}) - |b + de^{-iq/2} + fe^{iq/2} + ge^{-iq} + he^{iq}|^{1/2}]. \quad (5)$$

In our previous study,¹⁶⁾ the soft mode branch of K_2SeO_4 was expressed by assuming $f = g = j = k = 0$, $h = 6$, $c = -0.8$, $d = 4.6 \sim 6.9$ and $b = 1.6 \sim 9.3$; smaller is b , softer is the phonon branch.

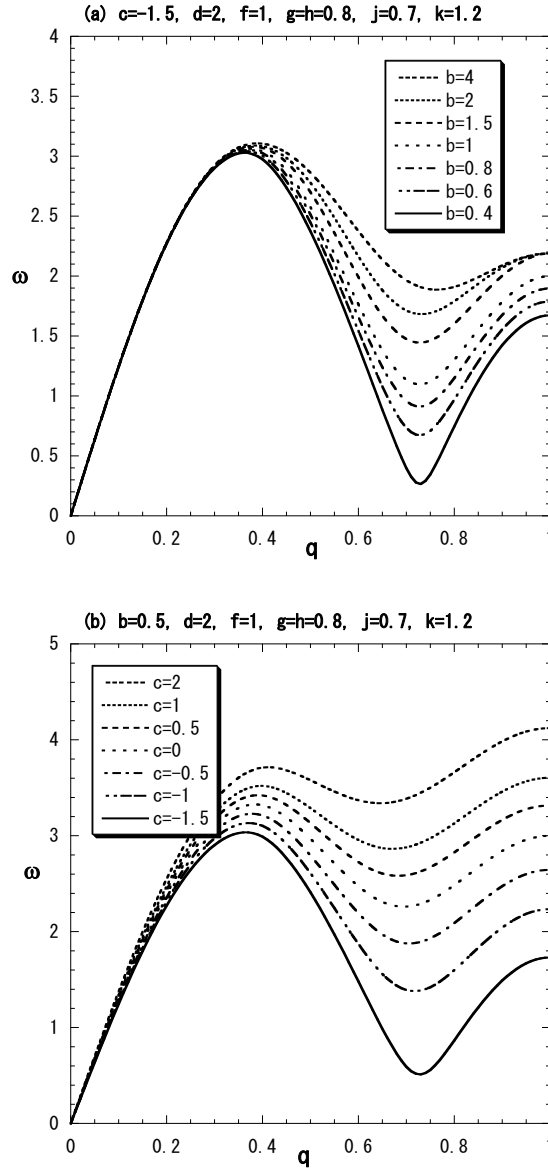


Fig. 7. Dispersion relation calculated for a one-dimensional model. The phonon branch becomes soft with decreasing (a) b , and (b) c .

Now let's consider the $(K_{1-x}Rb_x)_2SeO_4$ mixed crystal system. The sublattice variables P_n and Q_n can be assigned to the most prominent displacement, the rotation of SeO_4 tetrahedron along the a -axis. The replacement of alkali ions at site 1 will change the coupling constant b within a hexagonal network. Meanwhile, alkali ions at site 2 will affect the interlayer coupling c .

With substituting Rb in K_2SeO_4 , K at site 1 is firstly replaced by Rb. Therefore we assume the parameter b becomes larger with replacement of K by larger Rb ion at site 1. Figure 7 (a) demonstrate the calculated dispersion curve with a fixed parameter set of $c = -1.5$,

$d = 2$, $f = 1$, $g = h = 0.8$, $j = 0.7$, $k = 1.2$ and only b is varying. With increasing b , the dispersion shows a remarkable hardening. This is correspondent to the decrease of the transition temperature, the effect of the Rb substitution. Further, the minimum position of the branch moves toward $q = 1$ for large b , which is also in accord with the real dispersion relation observed by neutron inelastic scattering experiment.⁹⁾

When the substitution ratio is more than 30 %, K at site 2 is also replaced by Rb. This will affect the interlayer interaction c . Figure 7 (b) shows how does the dispersion relation change with the parameter c ; fixed parameters are $b = 0.5$, $d = 2$, $f = 1$, $g = h = 0.8$, $j = 0.7$ and $k = 1.2$. As c increases the bottom of the dispersion rises. In actual crystals with $x > 0.3$, it is considered that both b and c increase and the crystal will not transform to the incommensurate phase any more. Thus the one-dimensional model can explain the experimental result qualitatively.

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References

- 1) J. D. Axe, M. Iizumi and G. Shirane: in *Incommensurate Phases in Dielectrics*, ed. R. Blinc and A. P. Levanyuk (North-Holland, Amsterdam, 1986) Vol. 2, p. 1.
- 2) M. Iizumi, J. D. Axe, G. Shirane and K. Shimaoka: Phys. Rev. B **15** (1977) 4392.
- 3) C. J. de Pater, J. D. Axe and R. Currat: Phys. Rev. B **19** (1979) 4684.
- 4) I. Takahashi, A. Onodera and Y. Shiozaki: Acta Crystallogr., Sect. C **43** (1987) 179.
- 5) A. Kalman, J. S. Stephens and D. W. J. Cruickshank: Acta Crystallogr., Sect. B **26** (1970) 1451.
- 6) I. Etxebarria, J. M. Perez-Mato and G. Madariaga: Phys. Rev. B **46** (1992) 2764.
- 7) H. Shigematsu, Y. Akishige, H. Mashiyama, T. Tojo, H. Kawaji, T. Atake and T. Matsui: J. Korean Phys. Soc. **46** (2005) 235.
- 8) H. Mashiyama: J. Korean Phys. Soc. **29** (1996) S419.
- 9) H. Shigematsu, Y. Akishige, T. Tojo, H. Kawaji, T. Atake and T. Matsui: J. Thermal Anal. Calorimetry, **81** (2005) 555.
- 10) T. Janssen: in *Incommensurate Phases in Dielectrics*, ed. R. Blinc and A. P. Levanyuk (North-Holland, Amsterdam, 1986) Vol. 1, p. 67.
- 11) Z. Y. Chen and M. B. Walker: Phys. Rev. B **43** (1991) 5634.
- 12) Y. Ishibashi and T. Janssen: J. Phys. Soc. Jpn. **69** (2000) 3870.
- 13) H. Mashiyama: J. Phys. Soc. Jpn. **60** (1991) 180.
- 14) S. Kumazawa, Y. Kubota, M. Takata and M. Sakata: J. Appl. Crystallogr. **26** (1993) 453.
- 15) R. D. Shannon: Acta Crystallogr., Sect. A **32** (1976) 751.
- 16) H. Mashiyama and H. Shigematsu: Ferroelectrics **268** (2002) 95.