STRUCTURAL CHANGE OF THE SURROUNDINGS OF K^+ IN K_2ZnBr_4 CRYSTAL ON THE MONOCLINIC-ORTHORHOMBIC PHASE TRANSITION

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In K_2ZnBr_4 crystal, the monoclinic phase with the Sr_2GeS_4-type structure ($P2_1/m$, Z=2) is transformed into the orthorhombic phase with the β-K_2SO_4-type structure (*Pmcn*, Z=4) above 470K (an α-β transition). This α-β transition is known to be a reconstructive one. The crystal structure of the orthorhombic phase is refined in order to investigate in detail the structural change on the phase transition. It is found that the structure of the surroundings of one of two independent K^+'s in the monoclinic phase is almost the same as the rotated structure of the surroundings of one of two independent K^+'s in the orthorhombic one. We also discuss the difference between the crystal structures of K_2ZnCl_4 (orthorhombic) and K_2ZnI_4 (monoclinic) and the corresponding structures of K_2ZnBr_4.

Keywords: K_2ZnBr_4; α-β transition; Sr_2GeS_4-type structure; β-K_2SO_4-type structure; crystal structure analysis

1. INTRODUCTION

It has been found in the compounds with the A_2BX_4-type chemical formula that there is a considerable difference between the phase transition sequence in the Rb_2ZnCl_4-group compounds and that in the compounds K_2ZnBr_4 and K_2CoBr_4 (abbreviated hereafter KZB and

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KCB, respectively).[1-4] The former compounds take the β-K_2SO_4-type structure (orthorhombic). They undergo successive phase transition from the normal phase (space group *Pmcn*, Z=4) to the incommensurate phase (modulation along the *c*-axis), followed by the ferroelectric commensurate phase (space group $P2_1cn$, Z=12).[5]

On the other hand, the latter compounds possess two crystal modifications (α- and β-modifications). The α-modification is stable at room temperature and takes the Sr_2GeS_4-type structure (monoclinic). In the α-modification, there is also a second order paraelectric-ferroelectric phase transition.[1, 2, 4] The transformation from the α-modification to the β-one (α-β transition)occurs at about 470K. This transition is the first-order reconstructive one.[3] The β-modification can be supercooled below room temperature, if the sample is cooled at the rate of about 10K/sec, for instance. In the supercooled state, the β-modification shows the same phase transition sequence as that in the Rb_2ZnCl_4-group compounds.[3]

We previously analyzed the crystal structure of the highest temperature phase of the β-modification (phase Iβ) in KZB in order to clarify the mechanism of the α-β transition.[6] The determined structure of phase Iβ was not fully accurate, since only isotropic thermal parameter for each atom was taken into account in the analysis owing to a small number of the diffraction intensities obtained. So we refine the crystal structure of phase Iβ again in order to investigate in detail the structural change on the α-β transition in KZB. We also discuss the difference between the crystal structures of both modifications in KZB and those of K_2ZnCl_4 (normal phase, orthorhombic) and K_2ZnI_4 (room-temperature phase, monoclinic).

2. EXPERIMENTAL

The preparation of the crystals and the specimen for X-ray diffraction of KZB was performed by the same method reported previously.[4, 6] X-ray diffraction intensities were collected at 593K within the error of 0.5K controlled by a hot air flow. The 409 independent reflections satisfied with $|F_o| \geq 3\sigma(|F_o|)$ were used in the analysis. Program AXS89 system [7] was used to refine the crystal structure. Atomic scattering factors and anomalous dispersion corrections were taken from International Tables for X-Ray Crystallography.[8] As the starting positional parameters of each atom, those previously reported[6] were used. In the block diagonal least-squares calculation, $wR^2=\Sigma w(|F_c|-|F_o|)^2/\Sigma w|F_o|^2$ was minimized with $w=1/\sigma^2(F_o)$ for each reflection. The lattice constants obtained at 593K are a=7.717(4)Å, b=13.367(5)Å, c=9.539(3)Å.

3. RESULTS AND DISCUSSIONS

Three models were applied to the crystal structure refinement. Model 1 is a displacive one where all atoms except Br(3) are placed on the mirror plane normal to the *a*-axis. Model 2 is a partially disordered model where only bromine atoms are assumed to be split atoms and other atoms are placed on the mirror plane. Model 3 is a fully disordered model where all atoms except zinc atom are assumed to be split atoms. In these models, model 2 is supported by the amount of the improvement of *R*-factor against the increase of refinement parameters and by the small distortion of the $ZnBr_4^{2-}$ tetrahedron. Least-squares calculation for model 2 converged at wR=0.0374. The residual values of the difference Fourier synthesis were $-3.1<\Delta\rho<1.9$ (e/Å^3). The positional parameters obtained are almost coincident with those reported previously.[6] However the deviation of the positional parameter is improved. Final atomic parameters are listed in Table 1. Projection of the structure viewed from the *c*-direction is shown in Fig. 1.

TABLE 1 Atomic coordinates ($\times10^4$) and equivalent thermal parameters with e. s. d.'s in parentheses at 593K. Fixed parameter is denoted by (*). In this table, the atomic coordinates for bromine atoms show one of two configurations related by mirror reflection normal to the *a*-axis.

Atom	*x*	*y*	*z*	B_{eq}(Å^2)
K(1)	2500(*)	901(9)	1290(9)	14.8(5)
K(2)	2500(*)	6803(5)	9902(10)	9.7(4)
Zn	2500(*)	4208(3)	2204(4)	5.5(1)
Br(1)	2041(9)	4267(4)	-245(4)	10.8(2)
Br(2)	3038(8)	5821(3)	3223(4)	9.7(2)
Br(3)	4857(10)	3128(4)	2882(6)	10.6(2)
Br(4)	-70(9)	3617(4)	3266(5)	9.0(2)

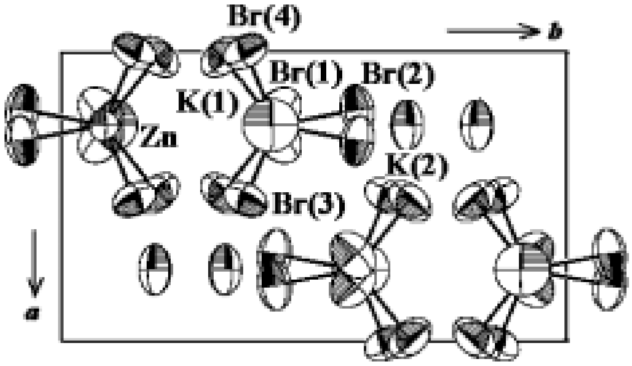

FIGURE 1 Projection of the crystal structure of KZB at 593K along the *c*-axis. The thermal parameters are shown by ellipsoids.

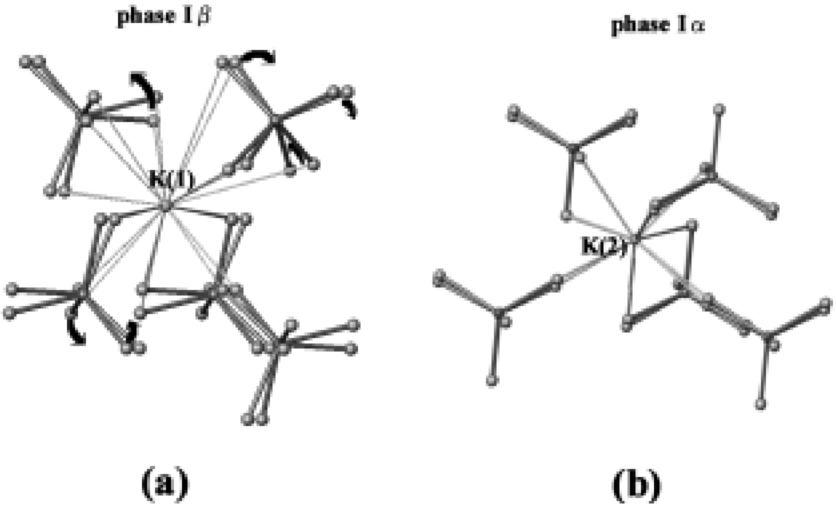

FIGURE 2 The local structures around $K(1)^+$ in phase Iβ (a) and $K(2)^+$ in phase Iα(b). The arrows in (a) indicate the rotational direction of the $ZnBr_4^{2-}$ tetrahedra to take the similar local structure around $K(2)^+$ in phase Iα.

In order to investigate the structural change of the surroundings of K^+ on the α-β transition in KZB, the detailed comparison of the structure of phase Iβ with that of phase Iα (room-temperature phase in the α-modification) was performed. It is found that the local structure around $K(2)^+$ in phase Iα is similar to that around $K(1)^+$ in phase Iβ. Though the coordination number of halogen atoms to K^+ is different from each other (8 for phase Iα, 11 for phase Iβ), both K^+'s are surrounded by 5 $ZnBr_4^{2-}$ tetrahedra. As shown in Fig. 2, if the $ZnBr_4^{2-}$ tetrahedra are rotated in the direction of arrows, the local structure around $K(1)^+$ in phase Iβ almost coincides that around $K(2)^+$ in phase Iα. Although the coordination numbers of halogen atoms to $K(1)^+$ in phase Iα and to $K(2)^+$ in phase Iβ are the same, 9, the local structures around these cations are quite different from each other. The number of the $ZnBr_4^{2-}$ tetrahedron around $K(1)^+$ in phase Iα is 4, while that around $K(2)^+$ in phase Iβ is 6. This difference indicates that large displacement of the $ZnBr_4^{2-}$ tetrahedron is required on the α-β transition.

We compare the structures around K^+ in KZB with those of the corresponding phases in K_2ZnCl_4 (β-structure)[11] and in K_2ZnI_4 (α-structure).[9] In these compounds, the kind of halogen atom is different from each other. The difference of the local structure around K^+ is hardly observable both in the α- and β-structures. Namely, the

TABLE 2 Structural data of some compounds with the A_2BX_4-type chemical formula. The (α) and (β) in the first column denote the Sr_2GeS_4-type structure and the β-K_2SO_4-type structure, respectively. The mark [*] in the second column denote the unpublished data. The C. N., *d* and *v* denote the coordination number of halogen atoms to the cation, the average distance from the cation to halogen atoms and the spherical volume around the cation calculated from the value of *d*, $v=4\pi d^3/3$, respectively.

	Compound	Cation	C. N.	d(Å)	v(Å^3)
(α)	K_2ZnBr_4[4]	K(1)	9	3.58	192.2
	(R. T.)	K(2)	8	3.53	184.3
(α)	K_2ZnI_4[9]	K(1)	9	3.85	239.0
	(R. T.)	K(2)	8	3.78	226.2
(α)	Rb_2ZnI_4[*]	Rb(1)	9	3.89	246.6
	(R. T.)	Rb(2)	8	3.87	242.8
(α)	Rb_2CdI_4[10]	Rb(1)	9	4.00	268.1
	(R. T.)	Rb(2)	8	3.91	250.4
(β)	K_2ZnBr_4	K(1)	11	3.93	254.3
	(593K)	K(2)	9	3.61	197.1
(β)	K_2ZnCl_4[11]	K(1)	11	3.73	217.4
	(588K)	K(2)	9	3.42	167.6
(β)	Rb_2CoBr_4[*]	Rb(1)	11	3.94	256.2
	(350K)	Rb(2)	9	3.63	200.4
(β)	$(NH_4)_2ZnBr_4$[12]	NH_4(1)	11	3.94	256.2
	(448K)	NH_4(2)	9	3.63	200.4

average distance from K^+ to halogen atoms only differs because of the different ionic radius of each halogen atom.

Table 2 shows the structural data of some compounds with the A_2BX_4-type chemical formula. As shown in this table, the spherical volume around $A(1)^+$ is about 4.7% larger than that around $A(2)^+$ in the same compound with the α-structure. On the other hand, in the compounds with the β-structure, the volume around $A(1)^+$ is about 28% larger than that around $A(2)^+$. This fact suits to the larger thermal parameter of $A(1)^+$ than that of $A(2)^+$. If relatively small A^+ was put into the $A(1)^+$ site with large volume, the crystal of the β-structure would not be stable. Relatively large A^+ compared to the size of the BX_4^{2-} tetrahedron may be required to realize the β-structure. Therefore, it is reasonable that, in the compounds with the Sr_2GeS_4-type structure, the existence of the α-β transition and the stability of the supercooled β-modification have been discussed from the point of view of the ratio the ionic radius of A^+ to the average bond length $B-X$ in the BX_4^{2-} tetrahedron.[6, 9, 10, 13]

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