X-ray diffraction, thermal analysis, and Raman scattering study of K_2BeF_4 and comparison to other members of the β-K_2SO_4 family with ferroelectric-paraelectric transitions

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Thermal analysis, powder diffraction, and Raman scattering as a function of the temperature were carried out on K_2BeF_4. Moreover, the crystal structure was determined at 293 K from powder diffraction. The compound shows a transition from $Pna2_1$ to $Pnam$ space group at 921 K with a transition enthalpy of 5 kJ/mol. The transition is assumed to be first order because the compound shows metastability. Structurally and spectroscopically the transition is similar to those observed in $(NH_4)_2SO_4$, which suggests that the low-temperature phase is ferroelectric. In order to confirm it, the spontaneous polarization has been computed using an ionic model. [S0163-1829(98)00309-9]

I. INTRODUCTION

Many compounds that are isostructural with β-K_2SO_4 in a certain temperature range, undergo phase transitions at lower temperatures. Some compounds even exhibit a cascade of several phase transitions, with the formation of incommensurately and commensurately modulated phases.[1] The most widely studied compounds of the family of β-K_2SO_4 are those showing phase transition, especially those with paraelectric-ferroelectric transition.[2,3] However, K_2BeF_4 is an exception; it was studied only by Mustafaev and co-workers,[4] who observed a phase transition from $Pn2_1a$ to $Pnam$ at 968 K. X-ray diffraction, thermal analysis, and Raman scattering studies on this compound have been carried out and the results are compared with those of the other compounds of the β-K_2SO_4 family.

II. EXPERIMENT

We were unable to obtain a single crystal of K_2BeF_4; it is due to its low solubility in an aqueous solution. Furthermore, the compound volatilized at 900 K when an open holder was used. Both of these difficulties limited the use of certain techniques to characterize the material and reduced the accuracy of those that could only be used with an open holder.

A. Synthesis

Potassium fluoroberyllate was obtained via the reaction $BeF_2 + H_2F_2 + K_2CO_3 = K_2BeF_4 + CO_2 + H_2O$ (BeF_2, H_2F_2, and K_2CO_3 were analytical grade). As quickly as a precipitate appeared, it was filtered and the filtered liquid ($pH = 7$) was left to evaporate at room temperature. After a few days, a polycrystalline powder was obtained, which was filtered and dried. The product was characterized by powder diffraction.

B. X-ray-powder diffraction

Powder-diffraction data were collected with a Siemens D500 automated diffractometer at different temperatures, using Cu $K\alpha$ radiation and a secondary monochromator. The experiment was a warming process from 298 K to 973 K, followed by a cooling process between the same temperatures. The cooling and warming rates were 10 K/min, and the sample was left for 10 min at measuring temperature, in order to stabilize the equipment and the sample. Measurements were taken at 298, 473, 673, and from 903 to 973, every 5 K. The step size was 0.025°, the time of each step 10 sec, and the 2θ range was 16°–120°. Cell parameters (Fig. 1) from powder diffraction were refined with the CELREF computer program.[5]

C. X-ray-structure determination

Diffraction data were collected at 298 K using Debye-Scherrer geometry, a 120° arch detector INEL and the sample in a rotating capillary to diminish preferred orientation. The radiation source was Cu $K\alpha$, using a primary pla-
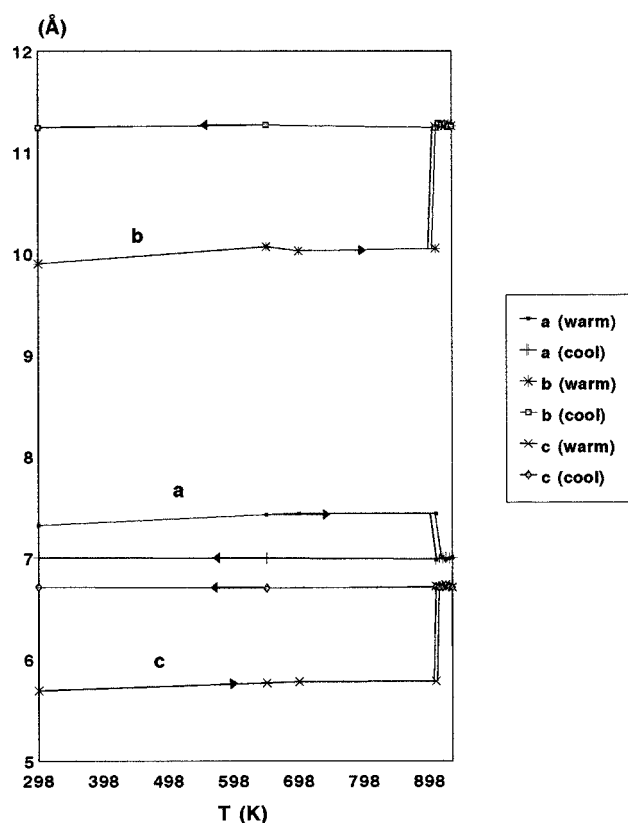
FIG. 1. Cell parameters and volume cell vs temperature, obtained from x-ray diffraction on powder samples.

TABLE I. Crystal data and structure refinement. [$R_{wp} = 100 \times \{\Sigma w_i (y_i - y_{0i})^2 / \Sigma w_i y_i^2\}^{1/2}$. $R_B = 100 \Sigma |I_0 - I_c| / \Sigma I_0$. S = goodness of fit $= R_{wp}/R_{expected}$. DWD = weighted Durbin-Watson statistic D.]

Empirical formula	K_2BeF_4
Formula weight	163.21
Crystal system	orthorhombic
Space group	$Pna2_1$
a (Å)	7.3067(5)
b (Å)	9.8856(7)
c (Å)	5.6910(4)
Volume (Å^3)	411.07(9)
Z	4
ρ (calculated) (Mg/m^3)	2.491
μ (mm^{-1})	2.217
F (000)	312
θ range (°)	10.5–100
N. of data	2725
Refl. collected	236
Refined parameters	36
R_{wp}	5.51
R_B	10.7
S	3.09
DWD	1.91

nar quartz monochromator. The time of exposure was defined by assigning a minimum count for the highest reflection (about 11 h).

Details of the structure determination at 298 K are listed in Table I. The unit-cell parameters were obtained using the TREOR computer program[6] and refined with the FULLPROF computer program.[7] The indexing of x-ray peaks indicates two possible space groups: $Pna2_1$ and $Pnam$. The structure was solved by direct methods using the SIRPOW computer program[8] and refined using the FULLPROF computer program.[7] The intensity statistic shows that the space group is $Pna2_1$, which was confirmed with the refinement. (Refinement, using the centrosymmetric group did not converge.) Beryllium and fluorines atoms were refined with an overall isotropic temperature factor; beryllium atom was constrained to be in the center of four fluorine atoms. A list of the final atomic coordinates is given in Table II.

D.   Raman scattering

Polarized Raman spectra were excited on the powder samples, using a Jobin Yvon T64000 spectrometer, and an argon ion laser excitation with fixed-time photon counting in 0.5 nm steps and a potential of 8 mW on the sample. Previous measurements with either the 488 or 514.5 nm λ values were carried out in order to determine the most accurate result. Finally the results were recorded with $\lambda = 488$ nm (the background increases with $\lambda = 514.5$ nm). The spectra were analyzed with three monochromator gratings and a spectral bandpass of 3 cm^{-1}. The detector used was a Control Data Corp. (CDC). The spectral range measured was 200–950

nm. All spectra were calibrated against selected neon lines. A Mettler FP84 sample warming cell was used in order to measure the spectra at different temperatures. Spectra at 941 K was measured on a metastable sample, warmed previously in a furnace and the metastability was corroborated by x-ray diffraction. The position, half width, and relative intensity of each peak was determined, assuming it to be a Lorentzian function (the Gaussian contribution is negligible).

E.   Thermal analysis

Differential thermal analysis (DTA) and thermogravimetric (TG) analysis were carried out with a NETZSCH 409, using a closed holder. The warming rate was 10 K/min, the temperature range 298–1000 K, the weight of the sample 94.7 mg, and the reference material was alumina. The weight of the sample did not decrease throughout the process.

III. RESULTS AND DISCUSSION

The results of DTA and TG analysis show that the K_2BeF_4 undergoes a phase transition with onset temperature

TABLE II. Atomic coordinates ($\times 10^4$) and equivalent isotropic B (Å^2).

	x	y	z	B (eq)
K(1)	1615(5)	936(4)	2500	3.19(11)
K(2)	−112(6)	6985(4)	2677(34)	4.16(12)
F(1)	3220(21)	3530(19)	245(33)	2.70(13)
F(2)	135(12)	4100(8)	2239(35)	2.70(13)
F(3)	3056(14)	5698(11)	2756(37)	2.70(13)
F(4)	2825(17)	3351(27)	4787(37)	2.70(13)
Be	2308(40)	4168(56)	2578(52)	2.70(13)
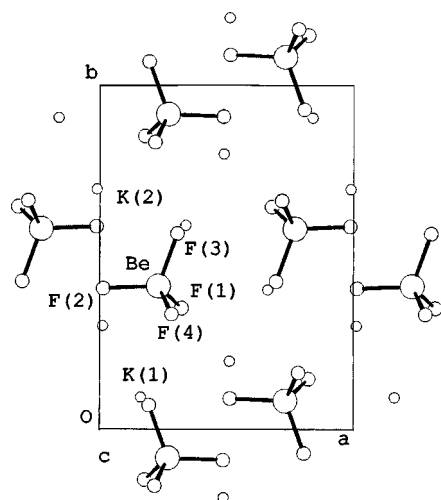
FIG. 2. Unit-cell content viewed down the *c* axis, showing the label of atoms.

TABLE III. Bond lengths (Å).

K(1)-F(2)i	2.576(10)	K(2)-F(4)vi	2.60(2)
K(1)-F(3)ii	2.72(2)	K(2)-F(3)	2.642(11)
K(1)-F(1)iii	2.841(16)	K(2)-F(3)vii	2.653(11)
K(1)-F(1)iv	2.850(19)	K(2)-F(4)ii	2.71(2)
K(1)-F(4)	2.86(3)	K(2)-F(1)viii	2.749(18)
K(1)-F(3)ii	3.01(2)	K(2)-F(2)viii	2.81(3)
K(1)-F(4)ii	3.01(3)	K(2)-F(2)	2.869(9)
K(1)-F(3)iii	3.065(11)	Be-F(4)	1.54(5)
K(1)-F(1)	3.097(18)	Be-F(2)	1.60(3)
K(1)-F(4)iii	3.141(16)	Be-F(3)	1.61(6)
K(2)-F(1)v	2.53(2)	Be-F(1)	1.61(4)

Symmetry code:

$$i = \tfrac{1}{2}+x, \tfrac{1}{2}-y, z$$
$$ii = \tfrac{1}{2}-x, -\tfrac{1}{2}+y, -\tfrac{1}{2}+z$$
$$iii = -\tfrac{1}{2}+x, \tfrac{1}{2}-y, z$$
$$iv = \tfrac{1}{2}-x, -\tfrac{1}{2}+y, \tfrac{1}{2}+z$$
$$v = \tfrac{1}{2}-x, \tfrac{1}{2}+y, \tfrac{1}{2}+z$$
$$vi = -x, 1-y, -\tfrac{1}{2}+z$$
$$vii = -\tfrac{1}{2}+x, \tfrac{3}{2}-y, z$$
$$viii = -x, 1-y, \tfrac{1}{2}+z$$

equal to 921 K in these experimental conditions. The ΔH is 5 kJ/mol. This value is higher than those observed in other compounds of the β-K_2SO_4 family; 3.9 kJ/mol at 223 K for $(NH_4)_2SO_4$;[9] 1.3 kJ/mol at 176 K for $(NH_4)_2BeF_4$, (Ref. 9) and 2.10^{-3} kJ/mol at 93 K for K_2SeO_4.[10]

Cell parameters were refined using all identified maxima (as the holder was open the number of used reflections changed from 35 reflections before heating the sample to 900 K to 24 reflections after heating). Peaks of two phases are observed from 903 to 913 K, so cell parameters of two phases were determined in this range. The transition was not produced during the cooling process in these experimental conditions, but a measurement at room temperature of the final sample after one day revealed that the metastable phase at room temperature had transformed to the stable phase. From that we conclude that the transition is of first order, while the phase transition for $(NH_4)_2SO_4$, $(NH_4)_2BeF_4$,[11] and K_2SeO_4 (Ref. 10) are second order. The *b* and *c* parameters increase in the transition from the low to the high-temperature phase, while the *a* parameter diminishes. This behavior is the same as that observed in the paraelectric-ferroelectric transition of the β-K_2SO_4 family of compounds.[11-13] Some authors hold the opinion that the direction *a* has an important role in the phase transitions, which occurs in some compounds of the family.[3,12-14] This analogy suggests that the high-temperature phase of K_2BeF_4 has the *Pnam* space group.

If we compare the solved crystal structure (Fig. 2) at 298 K with those of $(NH_4)_2SO_4$ (Ref. 15) at 209 K, it can be observed that the *a/c* ratio of ammonium sulfate is greater than those observed in potassium fluoroberyllate. This is consistent with the results of $(NH_4)_2(BeF_4)_x(SO_4)_{1-x}$,[11] in which the substitution of the ion sulfate by the ion fluoroberyllate produces an increase in this ratio. Moreover, the *a/b* ratio observed in the $(NH_4)_2SO_4$ is greater than those observed in the K_2BeF_4 which agrees with the results of the mixed crystals $(NH_4)_xK_{2-x}SO_4$ (Ref. 13) or $(NH_4)_xK_{2-x}SeO_4$,[16] where the substitution of K^+ by NH_4^+ produces an increase in this ratio. The relative position of the Be and S and the K and N atoms is the same in both structures (the lengths are different due to the size of the ions).

The main difference between the two structures is in the orientation of BeF_4 and SO_4 ions. In the fluoroberyllate compound the tetrahedron is turned 11° around the Be-F(2) bond and 3.6° around the crystallographic *c* axis with respect to the orientation of the SO_4 ion in $(NH_4)_2SO_4$ at 209 K. This produces differences in the coordination lengths of the K ion with respect to those of the NH_4 ion (Table III). The different orientation of SO_4 and BeF_4 ions in compounds of the β-K_2SO_4 family was observed in the mixed crystals of $(NH_4)_2(BeF_4)_x(SO_4)_{1-x}$.[11]

The complete list of Raman peak frequencies, width at half height, and the intensity at different temperatures are given in Table IV. The Raman spectrum of the β-K_2SO_4 family of compounds has been studied from experimental results and from the semiempirical rigid-ion model.[14,17,18] In this, the spectrum is divided into two parts: the external mode spectrum below 400 cm^{-1} and the internal mode spectrum above this value. The two lowest frequency peaks are assigned to translational motion of K ions (there are two K ions with different coordination polyhedra in the crystal structure). The lowest frequency is assigned to translational motion of the K(2) ion and the 392 cm^{-1} to the K(1) ion. The two peaks in the internal mode spectrum are assigned to ν_2 and ν_4 modes of BeF_4 by comparison with the free ion frequencies. The low intensity of the second frequency impeded the study of the variation of this mode as the temperature rises.

In general, the frequency of all peaks decreases and the width increases as temperature rises, which is due to the thermal dilatation of the crystal. The width of peaks decreases at 941 K, which is consistent with the assumption of *Pnam* space group in the high-temperature phase. The stretching $\nu_2(BeF_4)$ mode at 564 cm^{-1} in the high-temperature phase drops to 560 cm^{-1} when the compound passes to the low-temperature phase. This has been observed

TABLE IV. Frequencies corresponding to a translatory external mode (predominantly K) and internal vibration of BeF_4^{-2} vs the temperature.

		298	373	473	941
	T (K)				
$\nu(K2)$	ν (cm^{-1})	267.8(4)	267.0(8)	272.1(9)	272.2(4)
	Half width (cm^{-1})	13(1)	15(2)	18(3)	10(1)
	Relative intensity	12(2)	12(1)	12(1)	13(1)
$\nu(K1)$	ν (cm^{-1})	391.7(2)	392.5(2)	389.7(4)	394.2(2)
	Half width (cm^{-1})	15.0(5)	12.0(7)	31(1)	14.6(5)
	Relative intensity	31(2)	28(1)	59(1)	40(1)
$\nu_1(BeF_4)$	ν (cm^{-1})	562.42(1)	562.70(2)	559.72(4)	564.37(1)
	Half width (cm^{-1})	5.59(4)	5.44(6)	9.2(1)	5.00(4)
	Relative intensity	100(1)	100(1)	100	100(1)
$\nu_2(BeF_4)$	ν (cm^{-1})	669.0(9)			
	Half width (cm^{-1})	6(2)			
	Relative intensity	1.6(4)			

in the paraelectric-ferroelectric transition of $(NH_4)_2SO_4$.[17]

The peak intensity of $\nu_{tr}(K_1)$ shows the greatest temperature dependence, while the remaining peak intensities are constant. This is consistent with the assumption that the ion occupying site 1 is responsible for this transition in the β-K_2SO_4 family of compounds.[13,16]

IV. CONCLUSIONS

We have shown that K_2BeF_4 undergoes a first-order phase transition at 921 K. This compound shows the space group $Pna2_1$ at low temperature and the variation of the cell parameters and the Raman spectrum vs the temperature shows that the behavior of K_2BeF_4 is similar to those observed in $(NH_4)_2SO_4$, so the space group at high temperature is $Pnam$.

All this suggests that the phase transition of K_2BeF_4 is paraelectric-ferroelectric. In order to verify the ferroelectric behavior at low temperature the polarization of K_2BeF_4 was computed using an ionic model and the atomic coordinates and cell parameters at room temperature. The value obtained is 27×10^{-6} C/cm^2. In order to confirm this value, the model was applied to the $(NH_4)_2SO_4$, using the atomic coordinates at 209 K. The value obtained with the ionic model was 0.76×10^{-6} C/cm^2, while the experimental value[19] was 0.62×10^{-6} C/cm^2. The difference in the polarization values is consistent with the correlation between the Curie temperature and the spontaneous polarization in the β-K_2SO_4 family of compounds. The values of T_c (K) and $P \times 10^6$ (C/cm^2) are, respectively, 93 and 0.065 for K_2SeO_4,[10] 168 and 0.19 for $(NH_4)_2BeF_4$,[19] and 223.5 and 0.62 for $(NH_4)_2SO_4$.[19]

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