COMPARATIVE STUDY ON THE STRUCTURE OF K_2ZnCl_4 CRYSTAL DETERMINED FROM SINGLE CRYSTAL AND POWDER X-RAY DIFFRACTION

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Abstract

Crystal structures of dipotassium tetrachlorozincateK_2ZnCl_4 (KZC)was determined by both single crystal x-ray diffraction (SXRD) and powder x- ray diffraction (PXRD) techniques. KZC single crystals were grown by slow evaporation method. The obtained structural inform from SXRD had approximately the same precision as the PXRD technique. In the structure refinement, final values of R and R_w indice converged to 0.076 and 0.184. Structure analyses revealed that KZC sample possess the slightly distorted $ZnCl_4$ tetrahedra.

Keywords: K_2ZnCl_4 single crystal, x- ray diffraction, structure analyses

Introduction

The technique of single-crystal X-ray diffraction is the oldest and most common crystallographic method for determining the structure of the molecules. Crystals of A_2BX_4 type compounds, where A is K, Rb, Cs, NH_4 ion, B is Zn, Co, Hg and X is Cl or Br, are known as ferroelectrics. They have a common sequence of phase transitions; with decreasing temperature, the paraelectric-orthorhombic normal phase (N) changes to the INC phase followed by the commensurate (COM) phase of three-fold cell dimension along the c-axis (ferroelectric/ antiferroelectric phases).The existence of an INC lattice instability in these compounds depend basically on the effective volume of the A cations compared with the size of the BX_4 tetrahedra[Bruker W, 2001].

Above 553K the structure of KZC is the normal phase (N) with orthorhombic space group Pmcn. Transition to INC phase occurs at 553K and INC phase is retained down to 403K. Between 403K and 145K, it shows ferroelectric COM phase with space group $P2_1cn$.KZC has a stable COM region even on the cooling branch [Farrugia L J , 2005]. The phase transition sequences were summarized as shown in Figure 1.

The low-temperature phase transition in KZC connected to the ordering process of $ZnCl_4$ tetrahedra is investigated by diffuse X-ray scattering techniques. X-ray studies assigned the INC-COM transition to $ZnCl_4$ tetrahedra rotation. The interplanar distances change weakly with the temperature [Leduc, Hedoux AM ,1998]. KZC has the orthorhombic structure and a ferroelectric activity below 403 K. In the present work, structure analysis on pure crystal shows the right occupancy of K ion in the unit cell corresponding to the ratio of KCl. In the present work, the crystallize in the orthorhombic with the space group $P2_1cn$ at room temperature [Matsunaga H, 1982].

In the present study, the procedure of single crystal growth of K_2ZnCl_4 from the growth solution, the effect of sample preparation on the crystal and lattice parameter [Nardelli M,1995]

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Materials and Methods

Single crystals of KZC were grown by the slow evaporation technique from an aqueous solution containing KCl was dissolved with excess $ZnCl_2$ at high temperature 100˚C. The reagents of KCl and $ZnCl_2$ were dissolved with stoichiometric ratio of 2:1 in water. The excess $ZnCl_2$ was 2 wt % for the present sample. Because $ZnCl_2$ is a highly hygroscopic material, excess of $ZnCl_2$ was found necessary to compensate the water content and to be sure of the chemical reaction stoichiometry (Sheldrick G M , 1997).The saturated solution was slowly evaporated at about 100˚Cfor a few months. After getting the crystals, these were recrystallized from mother solution to afford colorless transparent single crystals of the title compound suitable for x- ray diffraction.

Powder X- ray Diffraction

Sample Preparation and Instrumentation

In an ideal PXRD experiment performed in a common Bragg-Brentano reflection geometry x-ray powder diffractometer, the sample should consist of powder particles of crystallite size between 0.1 and 1.0 micrometers. The sample should be packed in a cavity-type sample holder and genteelly pressed to a void preferred orientations. The sample surface should be big enough to ensure that the incident beam impinges over the sample in the full angular measuring range. Furthermore, the sample should be thick enough to ensure that the whole incident x-ray beam interacts with the sample and does not pass through it.

An x-ray powder diffractometer consists basically of a goniometer with a sample stage in its centre, the x-ray tube and the incident beam optics in its primary arm and the diffracted beam optics and a detector in its secondary arm. The goniometer is normally inside a shielded cabine in the upper part of a console. The x-ray generator and the measuring and control electronics are in the bottom part.

The phase formation of KZC sample were characterized by powder X- ray diffraction technique using Rigaku MultiFlex 2 kW type X-ray Diffractometer with Cu-K_α radiation (λ = 1.5404 Å) operating at 40 kV.

Single Crystal X- ray Diffraction

Sample Preparation and Data Collection

The samples are unfracturated and optically clear single crystals. Their size should be between 0.1 and 0.3 mm in the three directions of space. They are normally selected using an optical microscope (x40) equipped with a polarizing attachment and observing if light extinguishes regularly every 90º when turning the stage of the microscope.

A selected crystal is fixed on the tip of a thin glass fiber using epoxy or cement, orina loop including specific oil, which fits into the goniometer head in the diffractometer. The crystal is then aligned along the beam direction. It is necessary to know the stability properties of the crystals. Crystals can be sensitive to light, air or moisture, or susceptible to loss of crystallization solvent. If so, a special treatment is required. For example, they can be mounted inside sealed glass capillaries or the data collection can be performed at low temperature.

X-ray single crystal study is carried out using the Siemens P4 Single Crystal Diffractometer. In this diffractometer, MoKα radiation of wavelength 0.71073 Å with the X-ray power of 40 kV × 40 mA was used. The specimens having single domain with clear optical axis were cut under a polarizing microscope and shaped as a sphere with a diameter 0.35mm.The unit cell parameters were determined by least- squares refinement of 25 reflections with the diffraction angles 2θ =10 ~ 30˚. Intensity measurements were carried out in the ω - scan mode.

The maximum 2θ in which intensity data were collected was 50.0˚. Three standard reflections were monitored after every hundred reflections to check the stability of the measurements. After processing the raw data, Lorentz and Polarization corrections were made. Ψ scan is applied for absorption correction. Positional parameters and individual isotropic temperature factors were refined by a full-matrix least-squares SHELXTL-97. Anisotropic displacement parameters were used for non-H atoms and an isotropic parameter for the H atom. The function minimized was $\Sigma w (|F_0| - |F_c|)^2$, $w = 1/\sigma^2(|F_0|)$. The two discrepancy factors are defined $R=\Sigma (|F_0| - |F_c|)/\Sigma |F_0|$ and $R_w=\{\Sigma w(|F_0| - |F_c|)^2/\Sigma w |F_0|)^2\}^{1/2}$, respectively.

Results and Discussion

Powder x- ray diffraction (PXRD) and single crystal x- ray diffraction (SXRD) studies were carried out on the grown crystals. The comparison between lattice parameters between a, b and c are experimentally determined.

Structural Analysis by Powder X- ray Diffraction

The x- ray diffraction pattern of KZC was shown in Figure 1. The peaks (311), (121),(601) and (031) were observed at 2θ values 17.258°, 19.058°,23.355 and 24.745° for KZC sample and found to have polycrystalline nature with orthorhombic structure with the preferential orientation along the (031) plane. In this research work, X-ray diffraction measurements are carried out for KZC sample to determine the size of the particles. The crystallite size of the particles was estimated from the XRD spectrum by applying the Scherrer formula,

$$g_{\text{crystallite}} = \frac{0.9\lambda}{D\cos\theta}$$

where, g = the crystallite size (nm) , λ = the wavelength of the X-ray beam($\lambda = 1.54056\,\text{Å}$), D = the full width at half maximum height (radian) and θ = the angle of diffraction(degree).The broadening is evaluated by measuring the width g in radians, at an intensity equal to half the maximum intensity (FWHM). Structural parameters of KZC powder sample was presented in Table 1.

Structural Analysis by Single Crystal X- ray Diffraction

Crystal data, data collection and structure refinement are shown in Table 2. Bond distances and bond angles of tetrachlorozincate ions in different crystals are shown in Table 3. Fractional atomic coordinates and equivalent isotropic displacement parameters are shown in Table 4.X-ray diffraction pattern of $K_2 ZnCl_4$ powder sample as shown in Figure 2.

The a- axis projection, the projection normal to (100),(010) and view normal to (001) of the structures of KZC are shown in Figure 3, respectively. A group consists of K atom and $ZnCl_4$

tetrahedron. One group lies on the mirror plane (z= 1/4) and another group on the mirror plane(z=3/4).

The data can be viewed as sections of a three dimensional reciprocal space plot as shown in Figure 4. X-ray Fourier map presents charge density distribution. XRD data are not always accurate enough to observe the positional parameters of some atoms and the nature of bonding between them. The Fourier map is used to obtain the distribution in the electron density around Zn atom that supports the covalent bond formation between Zn and Cl atoms.2-D contour map view around two $ZnCl_4$ groups as shown in Figure 5.

Table 1 Lattice parameters and crystallite sizes of KZC crystal

Reflection plane (hkl)	d (Å)	2θ (deg)	FWHM (rad) × 10^{-3}	Lattice parameters (Å)			Crystallite size (nm)
				a	b	c	
(311)	5.1341	17.258	4.67	26.7288	12.4193	7.2823	30.03
(121)	4.6529	19.058	4.15	26.7288	12.4193	7.2823	33.88
(601)	3.8057	23.355	5.93	26.8006	12.4193	7.2693	23.88
(031)	3.5949	24.745	5.88	26.9108	12.4193	7.2497	24.14
Average				26.7975	12.4193	7.2709	27.98

Table 2 Model summary concerning unit cell information for KZC crystal

Crystal Data	
Chemical Formula	K_2ZnCl_4 (KZC)
Cell axes [A°]	a= 7.245 Å b= 12.395 Å c= 26.7707 Å
Cell angles [deg]	α = 90°, β = 90°, γ = 90°
Cell Volume[$A°^3$]	2404.03
Crystal system	Orthorhombic
Space group	$P2_1cn$
F(000)	1631.8
Density[gcm^{-3}]	2.37
Formular Weight	285.4
No.form.units Z	12
Abs.coeff: [mm^{-1}]	5.327
Chemical Formula	K_2ZnCl_4 (KZC)

Data Collection	
Instrument Description	Siemens SMART CCD area- detector diffractometer
Absorption correction	Ψ scans
Total reflections	16945
Unique reflections	1446
Reflections I>2σ(I)	1395

Refinement	
Cell refinement	Least squares method
R1	0.076
Rw	0.184
Goodness of Fit (S)	1.155

Table 3 Bond distance and bond angles of $ZnCl_4$ in KZC single crystal at room temperature

Atom	A	B	Distance	Atom	A	B	Distance
	Zn1	Cl6	2.251		Zn2	Cl17	2.226
	Zn1	Cl12	2.215		Zn2	Cl21	2.275
	Zn1	Cl15	2.241		Zn3	Cl5	2.289
	Zn1	Cl16	2.242		Zn3	Cl7	2.240
	Zn2	Cl13	2.273		Zn3	Cl8	2.262
	Zn2	Cl14	2.241		Zn3	Cl9	2.238

Atom	A	B	C	Angle	Atom	A	B	C	Angle
	Cl12	- Zn1	-Cl15	116.26		Cl14	- Zn2	- Cl13	107.34
	Cl12	- Zn1	-Cl16	109.62		Cl14	- Zn2	- Cl21	109.73
	Cl12	- Zn1	- Cl6	110.58		Cl13	- Zn2	- Cl21	105.18
	Cl15	- Zn1	-Cl16	106.08		Cl7	- Zn3	- Cl8	113.26
	Cl15	- Zn1	- Cl6	106.48		Cl7	- Zn3	- Cl9	114.97
	Cl16	- Zn1	- Cl6	107.39		Cl8	- Zn3	- Cl9	108.83
	Cl17	- Zn2	-Cl14	114.37		Cl5	- Zn3	- Cl7	106.30
	Cl17	- Zn2	-Cl13	105.72		Cl5	- Zn3	- Cl8	104.42
	Cl17	- Zn2	- Cl21	113.79		Cl5	- Zn3	- Cl9	108.38

Table 4 Fractional atomic coordinates and temperature factors ($x10^4$ $Å^2$) for all non-hydrogen atoms (Estimated Standard Deviations are given in parentheses)

$U_{eq}= (1/3)\sum_i\sum_j U_{ij}a^*_i a^*_j a_i a$

Atoms	x	y	z	Ueq
K1	1.91932	-0.18743	0.83196	0.04499
K2	1.40373	0.1866	0.83427	0.04685
K3	0.41926	.58334	0.78970	0.06268
K4	1.85166	-0.31190	0.99868	0.03737
K5	1.38023	-0.08457	0.62140	0.07671
K6	1.85873	0.0822	1.04322	0.07483
Zn1	1.86548	0.08182	0.90546	0.03216
Zn2	1.40648	-0.08210	0.75986	0.02910
Zn3	0.39438	0.58027	0.92767	0.0286
Cl5	0.65354	0.64486	0.88895	0.05602
Cl6	1.83365	-0.07840	0.94409	0.07897
Cl7	0.46908	0.55798	1.00819	0.04580
Cl8	0.3328	0.42338	0.88787	0.05170
Cl9	0.16264	0.69577	0.91360	0.05968
Cl12	1.83323	0.06319	0.82363	0.06068
Cl13	1.14153	-0.14015	0.72316	0.05449
Cl14	1.62557	-0.20467	0.74331	0.05686
Cl15	2.13396	0.15130	0.93177	0.09852
Cl16	1.64444	0.19122	0.93493	0.09200
Cl17	1.34061	-0.06388	0.84064	0.06257
Cl21	1.47578	0.07608	0.72107	0.04772

COM	COM ($P2_1cn$)	INC	N (Pmcn)
	145K	403K	553K

Figure 1 Phase transition sequence of KZC crystal.

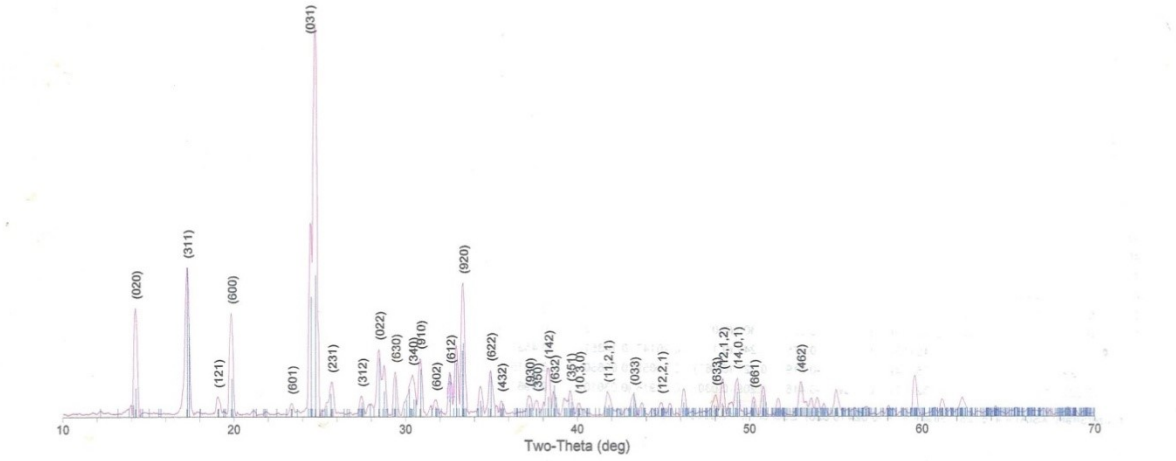

Figure 2 X-ray diffraction pattern of KZC crystal

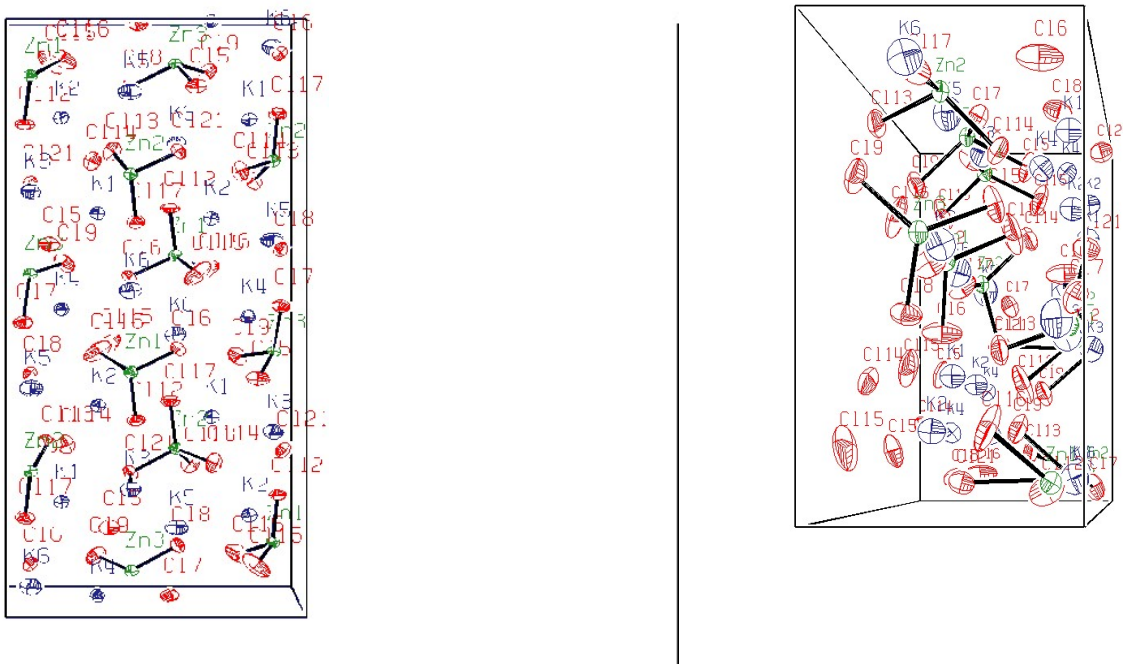

Figure 3 Projection normal to (100), (010)and (001) of the structure of KZC crystal

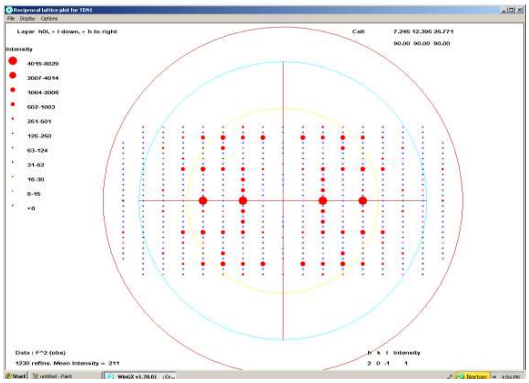

Figure 4 Reciprocal Lattice Plot for KZC crystal

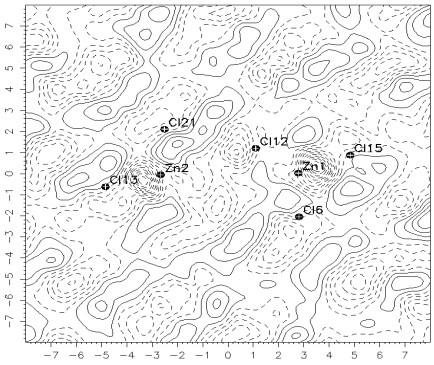

Figure 5 2-D Contour Map View of two $ZnCl_4$ groups

Conclusion

The XRD results of showed the pure crystal KZC is a sort of solid solution right occupancy of K ion in the unit cell according to the mixing molar ratio. The K ion form linear chain whose periodicity is incommensurate with that of the arrangement of the $ZnCl_4$ tetrahedron. The Zn atom shifts away from one of Cl atoms in the tetrahedral molecules and carries an electric dipole moment parallel to the Zn-Cl bond. The comparison between lattice parameters between a, b and c are experimentally determined. The observed lattice parameter a, b and c found to be 26.7975 Å, 12.4193 Å, 7.2709 Å in KZC sample for PXRD and 7.2452 Å, 12.3953 Å, 26.7707 Å for SXRD, respectively. The average value of crystallite size is calculated as 27.98 nm.

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