

## SHORT COMMUNICATIONS

**Experimental (155 K) and predicted (151 K) Curie temperature ( $T_c$ ) of  $K_2ZnBr_4$ : structural confirmation of ferroelectric state below  $T_c$ .** By S. C. ABRAHAMS, *Physics Department, Southern Oregon State College, Ashland, OR 97520, USA*

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## Abstract

The temperature  $T_c$  at which  $K_2ZnBr_4$  is predicted to transform from the paraelectric to the ferroelectric phase is 151 (19) K, based on the crystal structure determinations at 291 and 144 K by Fábry, Breczewski, Zúñiga & Arnaiz [*Acta Cryst.* (1993). C49, 946–950] and the Abrahams–Kurtz–Jamieson relationship. A dielectric and heat-capacity anomaly in this material at 155 K has been reported elsewhere. The locations reported for the  $ZnBr_4^{2-}$  and  $K^+$  ions fulfill the requirements of mirror plane symmetry above  $T_c$ ; ionic displacements along the polar direction that approach but do not exceed 0.1 Å and that violate the mirror symmetry on cooling through  $T_c$  form the basis of the prediction and satisfy the structural criteria for ferroelectricity in the phase below the transition.

## Introduction

The crystal structure of  $K_2ZnBr_4$  at 291 and 144 K was determined by Fábry, Breczewski, Zúñiga & Arnaiz (1993) following the report by Shimizu, Yamaguchi, Suzuki, Takashige & Sawada (1990) that small dielectric and endothermic anomalies appear in this material at 155 K. Asymmetric reversal of the pyroelectric polarization and unsuccessful attempts at observing dielectric hysteresis below this temperature opens the inference that  $K_2ZnBr_4$  may undergo a paraelectric–ferroelectric phase transition to question: an alternative interpretation of the transition is from paraelectric to antiferroelectric, with a field-induced pyro- or ferroelectric state. The 1993 structural determinations allow application of the AKJ relationship (Abrahams, Kurtz & Jamieson, 1968) and the structural criteria of Abrahams (1988) to a potentially ferroelectric crystal. The AKJ relationship has been used earlier as an indicator of ferroelectricity in structures containing tetrahedral ions located on trigonal axes and as a predictor for the value of  $T_c$  corresponding to the subsequent transition observed on heating to the paraelectric phase (Abrahams, 1990); it has not been applied previously to the case of a crystal that contains tetrahedral ions in general positions for which both atomic coordinates and an experimental transition temperature are available. The number of confirmed or potentially ferroelectric structures with tetrahedral ions in general positions is large, making a successful application to the present case of considerable interest. The AKJ relationship in (1) gives  $T_c$  as a function of the largest displacement  $\Delta y$ , from the zero spontaneous polarization structure, along the polar direction by the

Table 1. Atomic coordinates ( $\times 10^4$ ) of  $K_2ZnBr_4$  at 144 K,\* measured (paraelectric)  $y'$  coordinates at 291 K and polar  $\Delta y$  displacements (Å)

$$a = 7.204 (3), b = 7.413 (4), c = 9.028 (5) \text{ \AA} \text{ and } \beta = 108.67 (3)^\circ$$

	$x$	$y$	$z$	$y'$	$\Delta y$
K(1)	7748 (5)	2450 (10)	5726 (4)	2500	–0.091
K(2)	7087 (5)	2450 (10)	467 (4)	2500	–0.091
Zn	2804 (2)	–2573 (6)	2050 (2)	2500	0
Br(1)	1029 (2)	2691 (6)	–693 (2)	2500	0.087
Br(2)	769 (2)	2656 (7)	3676 (2)	2500	0.062
Br(3)	4929 (4)	–18†	2618 (3)	–18 (1)	–0.087
Br(3A)	5093 (4)	5046 (3)	2681 (3)	5018‡	0.087

\* All measured atomic coordinates are taken from Fábry, Breczewski, Zúñiga & Arnaiz (1993).

† This coordinate has been rounded to four significant figures, see text.

‡  $y'[\text{Br}(3A)] = 1/2 - y'[\text{Br}(3)]$  in space group  $P2_1/m$ . Br(3A) is equivalent to Br(3) above and independent of Br(3) below  $T_c$ .

metal ion that forms the strongest and least ionic bonds in the ferroelectric structure

$$T_c = (\mathcal{N}/2k)(\Delta y)^2 K, \quad (1)$$

where  $\mathcal{N}$  is a characteristic force constant,  $k$  is Boltzmann's constant,  $\mathcal{N}/2k \approx 2.0 \times 10^4 \text{ K \AA}^{-2}$  and  $b$  is the polar axis. This displacement may be identified in  $K_2ZnBr_4$  as  $\Delta y_{\text{max}}[\text{Zn}]$ .

#### Determination of atomic displacements and predicted $T_c$ in polar $K_2ZnBr_4$

$K_2ZnBr_4$  is isomorphous with  $\text{Sr}_2\text{GeS}_4$  at room temperature, in space group  $P2_1/m$ . The  $ZnBr_4^{2-}$  ion forms a distorted tetrahedron with Zn, Br(1) and Br(2) situated on the mirror plane at  $y = 1/4$  and two equivalent Br(3) atoms close to  $y = 0$  and  $1/2$ . A consequence of the mirror plane is a restriction of the  $ZnBr_4^{2-}$  ion dipole to this plane; the inversion center causes all dipoles within the entire unit cell to cancel above  $T_c$ . Elimination of the mirror plane at the phase transition results in the atomic coordinates of Table 1, as given by Fábry, Breczewski, Zúñiga & Arnaiz (1993) but with  $y[\text{Br}(3)]$  taken as  $-0.0018$  rather than the value  $-0.001786$  chosen by these authors for fixing the origin. It may be seen, from Table 1, that  $y[\text{Br}(1)]$  and  $y[\text{Br}(2)]$  are displaced from  $y[\text{Zn}]$  at temperatures below  $T_c$  by  $\Delta y = 0.0118$  and  $0.0083$ , respectively. Above  $T_c$ ,  $y[\text{Br}(3)] - y[\text{Zn}] = y[\text{Zn}] - y[\text{Br}(3A)]$ ; below  $T_c$ , the difference between the right and left sides of this equality gives the corresponding polar  $\Delta y$  displacement for Br(3) as  $-0.0118$  and

that for Br(3A) as 0.0118. The choice of origin is arbitrary in polar space groups, hence these relative displacements are equally attributable to Zn. The *largest* relative displacement by Zn along the polar axis is thus 0.0118, *i.e.* 0.087 Å. Substitution of  $\Delta y = 0.087$  Å in (1) gives the predicted value of  $T_c$  as 151 K. The e.s.d. in atomic  $y$  coordinates determined by Fábry, Brezowski, Zúñiga & Arnaiz (1993), see Table 1, corresponds to an e.s.d. in  $T_c$  of about 19 K. The experimental transition temperature 155 K is indistinguishable from the predicted value of  $T_c = 151$  (19) K. It may be noted that  $y$  coordinates only need be considered in this application of the AKJ relationship, since all net dipoles arising from  $\Delta x$ ,  $\Delta z$  displacements are necessarily zero in  $K_2ZnBr_4$ , both below and above  $T_c$ .

#### Structural confirmation of ferroelectricity in $K_2ZnBr_4$ below $T_c$

Dielectric measurement and differential thermal analysis can provide important information about a phase transition and can show that it may be associated with a dielectric anomaly. In the absence of additional proof, however, *e.g.* that dielectric hysteresis occurs at the phase transition, the inference that a phase transition exhibiting such an anomaly is from paraelectric to ferroelectric rather than to another state necessarily remains unconfirmed. The space-group change from  $P2_1/m$  to  $P2_1$  on cooling through  $T_c$  is consistent with a second-order phase transition. The order parameter at a second-order phase transition determines the magnitude of the resulting atomic displacements and polyhedral ion rotations from the locations above the transition temperature (Ihringer & Abrahams, 1984). The characteristics of the order parameter in

$K_2ZnBr_4$  at  $T_c$  may be investigated experimentally by measurement of the lattice parameter and structural thermal dependences. If the primary structural rearrangement at  $T_c$  is fully described by a phase transition in which all zero-valued  $\Delta y$  above the transformation take on the magnitudes given in Table 1 then, since all displacements have the same chance of assuming the opposite sense in a ferroelectric crystal, the corresponding entropy change at  $T_c$  is expected to be  $R \ln 2 = 5.76 \text{ J K}^{-1} \text{ mol}^{-1}$ .

The polar displacements given in Table 1, derived from the structures determined by Fábry, Brezowski, Zúñiga & Arnaiz (1993), may be considered to lie within the normal range for low  $T_c$  ferroelectrics as also does the rotation of less than  $3^\circ$  by the  $ZnBr_4^{2-}$  ion. The structural criteria presented by Abrahams (1988) predict a ferroelectric phase in any pyroelectric crystal that has atomic displacements along its polar axis no greater than about 1 Å from the paraelectric positions and in which the largest such displacement by the atom forming the strongest and least ionic bonds is greater than about 0.1 Å. These criteria are fully satisfied in the case of  $K_2ZnBr_4$ , thereby providing confirmation that this crystal is ferroelectric below  $T_c$ .

#### References

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