

## Crystal Structure of $\text{Cs}_2\text{KTbCl}_6$ and $\text{Cs}_2\text{KEuCl}_6$ by Powder X-Ray Diffraction

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$\text{Cs}_2\text{KTbCl}_6$  and  $\text{Cs}_2\text{KEuCl}_6$  from the elpasolite family ( $A_2BLnX_6$ ) were obtained by slowly evaporating to dryness a hot aqueous HCl solution of the appropriate chlorides and characterized by powder X-ray diffraction. Using WYR3 program software it was found that the title compounds are cubic and isostructural to  $\text{Rb}_2\text{NaTmCl}_6$ . Cell parameters for  $\text{Cs}_2\text{KTbCl}_6$  and  $\text{Cs}_2\text{KEuCl}_6$  are  $a = 11.1224(3)$  Å and  $a = 11.1633(3)$  Å, respectively. The space group for both compounds is  $Fm\bar{3}m$ . © 1997

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### INTRODUCTION

The elpasolites form an interesting family of cubic symmetry compounds. The spectroscopic, magnetic, and electric properties of the cubic elpasolite system have been the subject of numerous studies reported over the past 20 years (1). One of the advantages is that they present  $\text{Ln}^{3+}$  ions located on sites of high symmetry, which is important when studying spectroscopic properties in the solid state. In most cases,  $\text{Ln}^{3+}$  ions are present in different symmetry sites and usually trivalent rare earth ions are not found in sites of octahedral symmetry (2), whereas in elpasolite compounds the lanthanide  $\text{Ln}^{3+}$  site is cubic with perfect octahedral symmetry, as is the case for monovalent *A* and *B* ions (3, 4). Excited states of lanthanide ions in centrosymmetric environments should have much longer relaxation times than those localized in noncentrosymmetric sites. This offers interesting possibilities for optical pumping and for energy storage and transfer (5). When substitutions take place in a crystalline compound, significant structural changes affecting chemical and spectroscopic properties are produced.

One of the most attractive possibilities for this system is that the spectroscopic phenomena are relevant to most lanthanide solid state derivatives, especially when the symmetry site they acquire is the appropriate one for fluorescence and similar events. Most elpasolites present

interesting spectroscopic properties when the octahedral sites of the cubic crystals are occupied by lanthanide ions, as they can be excited to diverse spectroscopic states (6). Europium and terbium are well known as easily excitable ions. In the case of the title compound one would expect an intrinsic fluorescence response in the visible region, due to the high octahedral symmetry of the sites they occupy in the crystal. The expected transitions could be for  $4f^n \rightarrow 4f^{n-1}5d$ . The significance of this possibility is to use these compounds as light absorbing-emitting devices. It is known that doping this system with other lanthanide ions improves the quantum yields and modifies the wavelength of the produced radiations (7). Although the differences in ionic ratio are not large for the lanthanide, they produce structural changes when the substitutions take place in a crystalline compound. These changes are significant when they affect chemical and spectroscopic properties.

To study their optical properties, we have synthesized two elpasolites which have been only scarcely described (8). We have also determined their crystal structure by powder X-ray diffraction using WYR3 software and the TREOR program (9). Here we present the complete crystallographic data of both compounds. Their electric and optical properties are under study in our laboratory.

### EXPERIMENTAL

$\text{Cs}_2\text{KTbCl}_6$  and  $\text{Cs}_2\text{KEuCl}_6$  were prepared by slowly evaporating to dryness a hot aqueous HCl solution of the appropriate chlorides. The reagents used were CsCl (99.99%),  $\text{TbCl}_3 \cdot 6\text{H}_2\text{O}$  (99.99%), and  $\text{EuCl}_3$  from Aldrich. Density measurements were made with specific gravity bottles using  $\text{CCl}_4$  as the displacement liquid.

The lattice parameters of the samples were determined with a Siemens D5000 powder diffractometer with  $\text{CuK}\alpha_1$  radiation, secondary graphite monochromator, and nickel filter, as fcc with  $a = 11.122(3)$  Å for terbium elpasolite and  $a = 11.1633(3)$  Å for the europium compound.

DIFFRACT/AT (10) was applied to obtain well-resolved powder lines. TREOR program (9) was used for the first indexing. No special extinctions could be recognized. The space group is  $Fm\bar{3}m$ . There are 19 reflections in the range  $2^\circ < 2\theta < 100^\circ$  with a step width of  $0.02^\circ$  for  $2\theta$  counting. The time per step was 5 s. The data were corrected using a Si standard external with  $a = 5.4306(4)$  Å at  $25^\circ\text{C}$  and subtracting  $K\alpha_2$  before reading the  $2\theta$  and intensity.

From the refinement a Rietveld method was applied with the WYR3 program (11). The employed profile was a pseudo-Voigt function. The final  $wR$  was 10.51 due to some impurities formed by the interaction with the air humidity. The determination of the powder crystal structure was based on the isostructural compound  $\text{Rb}_2\text{NaTmCl}_6$  and for the performance of our structure with WYR3 program was used.

### RESULTS AND DISCUSSION

Two compounds of the elpasolite family ( $A_2BLnX_6$ )  $\text{Cs}_2\text{KTbCl}_6$  and  $\text{Cs}_2\text{KEuCl}_6$ , were obtained and character-

**TABLE 1A**  
X-Ray Diffraction Data for  $\text{Cs}_2\text{KTbCl}_6$

$2\theta$ ( $^\circ$ )	$d$ (Å)	$I/I_0$	$h$	$k$	$l$
13.786	6.423	34	1	1	1
22.593	3.935	100	2	2	0
26.557	3.356	9	3	1	1
27.756	3.214	11	2	2	2
32.175	2.782	83	4	0	0
35.150	2.553	1	3	3	1
39.679	2.271	55	4	2	2
42.198	2.1415	8	5	1	1
46.132	1.9676	40	4	4	0
48.375	1.8815	5	5	3	1
51.966	1.7596	13	6	2	0
54.025	1.6973	1	5	3	3
54.712	1.6776	4	6	2	2
57.364	1.6062	10	4	4	4
59.275	1.5589	3	5	5	1
62.462	1.4868	15	6	4	2
64.259	1.4495	< 1	7	3	1
67.317	1.3909	3	8	0	0

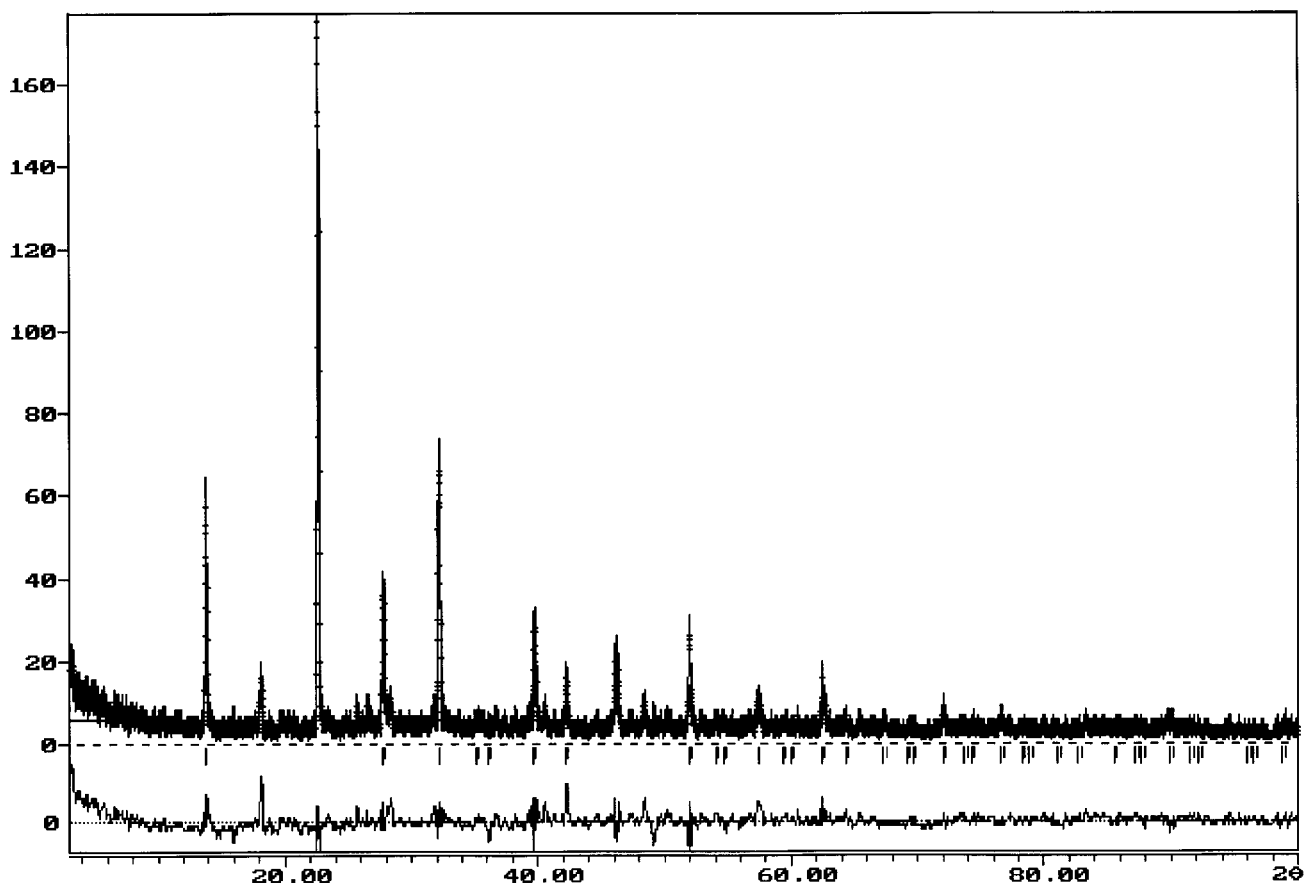


FIG. 1. X-ray refined powder diffraction pattern for  $\text{Cs}_2\text{KTbCl}_6$ .

**TABLE 1B**  
X-Ray Diffraction Data for Cs<sub>2</sub>KEuCl<sub>6</sub>

$2\theta$ (°)	$d$ (Å)	$I/I_0$	$h$	$k$	$l$
13.742	6.44	32	1	1	1
22.584	3.937	100	2	2	0
26.328	3.385	9	3	1	1
27.687	3.221	10	2	2	2
32.078	2.790	80	4	0	0
35.037	2.561	1	3	3	1
39.547	2.279	53	4	2	2
42.058	2.148	8	5	1	1
45.989	1.973	39	4	4	0
48.227	1.887	5	5	3	1
51.792	1.765	12	6	2	0
53.850	1.7024	1	5	3	3
54.529	1.6828	4	6	2	2
57.181	1.6109	9	4	4	4
62.248	1.4914	14	6	4	2
64.090	1.4529	< 1	7	3	1
67.087	1.3951	3	8	0	0

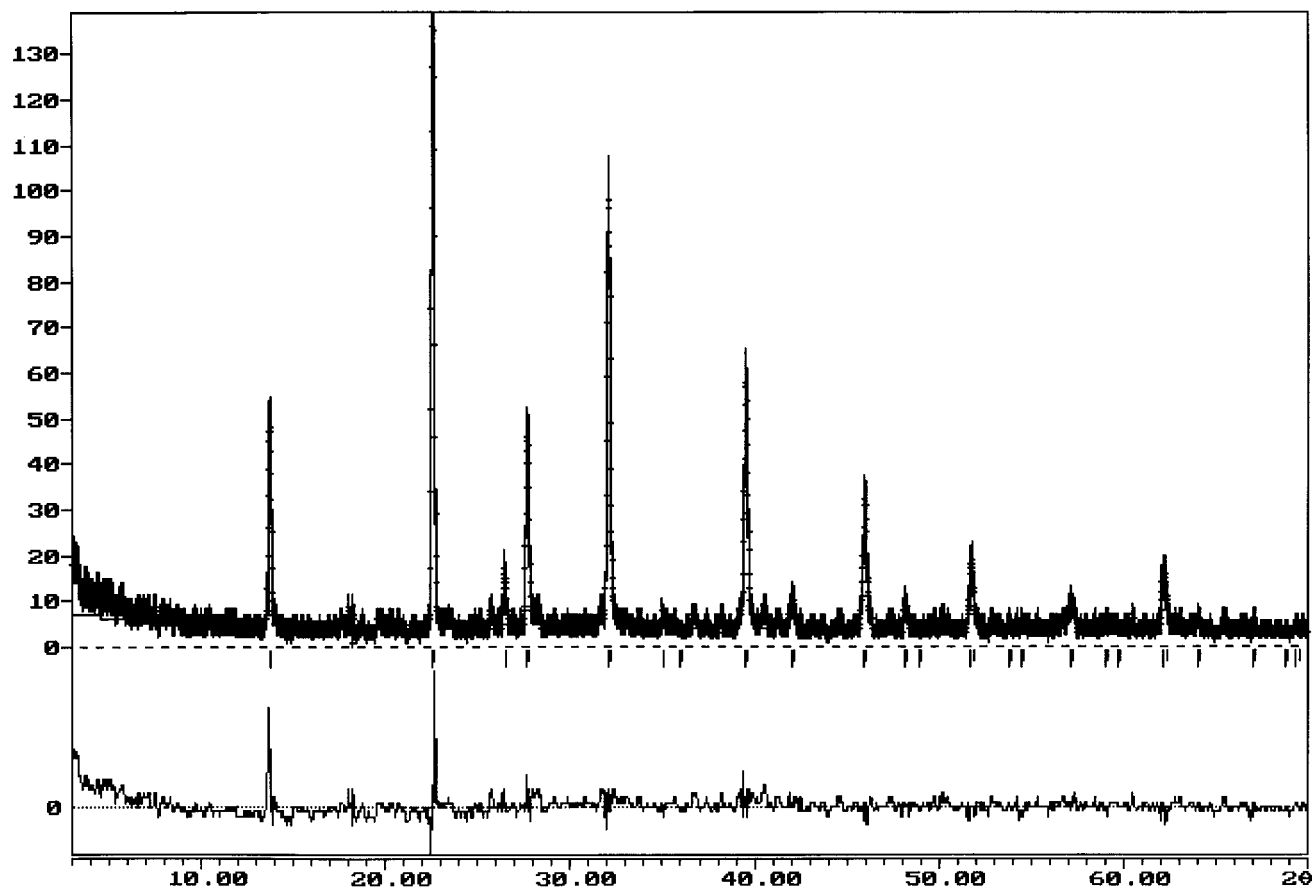
**TABLE 2A**  
Atomic-Positions of Cubic Cs<sub>2</sub>TbCl<sub>6</sub> ( $Fm\bar{3}m$ )

Atom	Site	$x$	$y$	$z$	$B(\text{Å}^2)$
Tb	4a	0	0	0	2.072(5)
Cs	8c	0.25	1/4	1/4	4.798(2)
K	4b	0.50	1/2	1/2	3.117(7)
Cl	24e	0.2257(11)	0	0	5.278(13)

ized by powder X-ray diffraction. The experimental data on interplanar spacing, relative intensities, and  $hkl$  indices of the phases are shown in Tables 1A and 1B. The powder diffractogram with  $I_{\text{obs}}$  (observed intensities),  $I_{\text{calc}}$

**TABLE 2B**  
Atomic-Positions of Cubic Cs<sub>2</sub>KEuCl<sub>6</sub> ( $Fm\bar{3}m$ )

Atom	Site	$x$	$y$	$z$	$B(\text{Å}^2)$
Eu	4a	0	0	0	0.990(2)
Cs	8c	0.25	1/4	1/4	2.070(7)
K	4b	0.50	1/2	1/2	2.190(4)
Cl	24e	0.2317(8)	0	0	5.980(3)

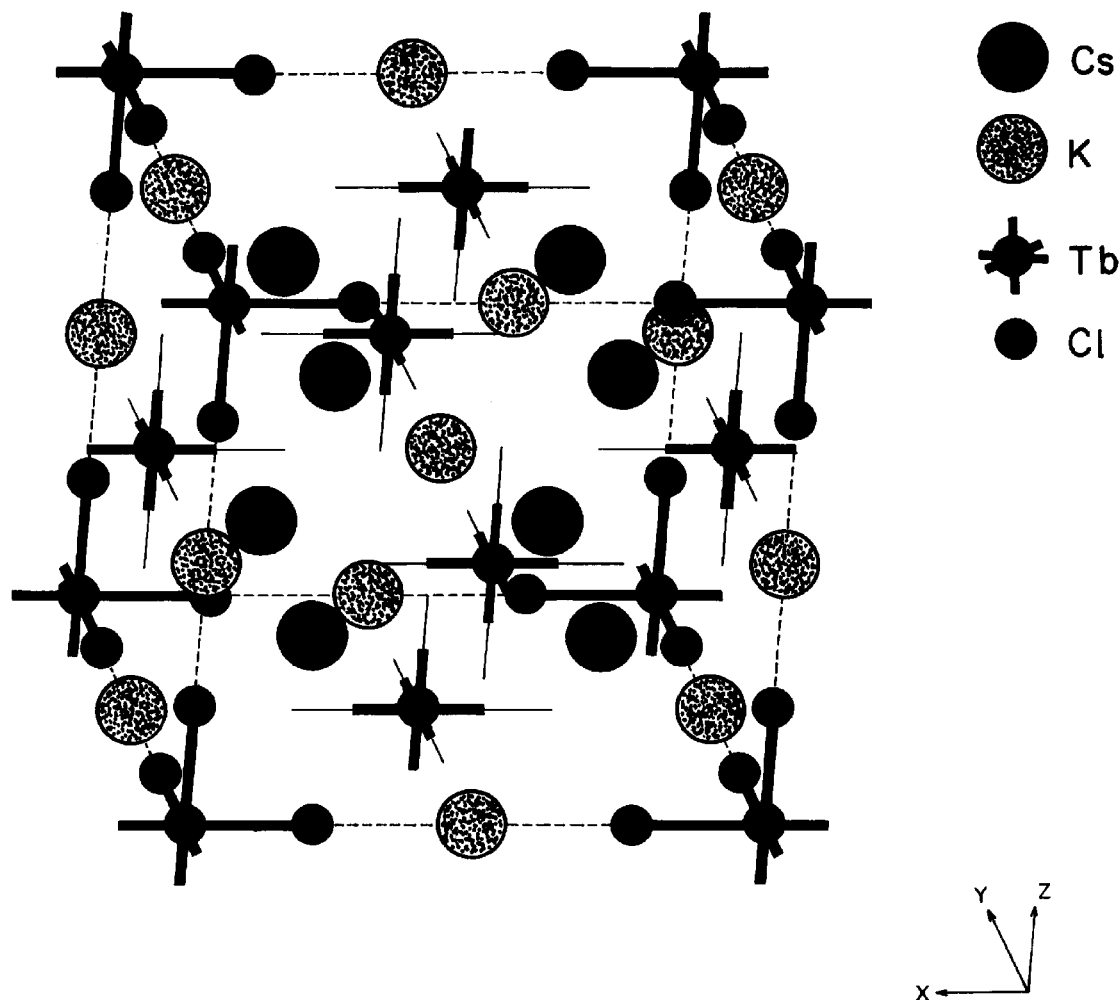


**FIG. 2.** X-ray refined powder diffraction pattern for Cs<sub>2</sub>KEuCl<sub>6</sub>.

**TABLE 3**  
**Bond Lengths (Å) and Angles (°) for Terbium Compound and the Europium Compound**

Terbium compound		Europium compound	
Tb-Cl	2.51(1)	Eu-Cl	2.586(8)
Cl-Cl	3.661(7)	Cl-Cl	3.718(1)
Cs-Cl	3.94(1)	Cs-Cl	3.952(8)
K-Cl	3.05(1)	K-Cl	2.995(8)
K-Cl'	2.969(7)	K-Cl'	2.943(1)
Cl'-Cl'	4.199(7)	Cl'-Cl'	4.163(1)
Cl-Tb-Cl	179.9(7)	Cl-Eu-Cl	180.0(9)
Cl-Tb-Cl	90.0(3)	Cl-Eu-Cl	90.0(4)
Cl-Cs-Cl	55.4(2)	Cl-Cs-Cl	56.2(3)
	64.4(1)		63.7(2)
	119.9(1)		119.9(3)
	174.4(2)		175.4(3)
	90.1(2)		90.0(3)
Cl'-K-Cl'	180.0(4)	Cl'-K-Cl'	180.0(8)
	90.0(3)		90.0(4)

(calculated intensities),  $I_{\text{diff}}$  (difference between  $I_{\text{obs}}$  and  $I_{\text{calc}}$ ), and  $I_{\text{mark}}$  (possible Bragg diffraction) are shown in Figs. 1 and 2. The impurities are evident in the observed pattern and they are excluded from the refinement. The compounds have perovskite related structure with the lanthanides and potassium atoms located in octahedral sites. In both compounds the  $\text{KCl}_6$  octahedron is larger than that of  $\text{LnCl}_6$  ( $d \text{ KCl} = 3.05(1) \text{ \AA}$ ,  $d \text{ TbCl} = 2.51(1) \text{ \AA}$  for  $\text{Cs}_2\text{KTbCl}_6$  and  $d \text{ KCl} = 2.995(8) \text{ \AA}$ ,  $d \text{ EuCl} = 2.586(8) \text{ \AA}$  for  $\text{Cs}_2\text{KEuCl}_6$ ). Cs is in a distorted dodecahedral site. The four CsCl distances of each compound are equal (CsCl 3.94(1) Å for the Tb compound and CsCl 3.952(8) Å for the Eu compound), but the ClCsCl angles are not equivalent (see Table 3). Both unit cells are isostructural, but that of  $\text{Cs}_2\text{KEuCl}_6$  is a little larger than that of  $\text{Cs}_2\text{KTbCl}_6$  ( $a = 11.163(3) \text{ \AA}$  and  $a = 11.122(3) \text{ \AA}$ , respectively) as can be expected due to the differences in ionic radii. Tables 2A and 2B give the refinement data of the crystallographic positions due to Rietveld analysis in both compounds. Table 3 shows



**FIG. 3.** Unit cell of  $\text{Cs}_2\text{KTbCl}_6$ .

**TABLE 4A**  
Crystallographic and Experimental Details for Cs<sub>2</sub>TbCl<sub>6</sub>

Cs <sub>2</sub> TbCl <sub>6</sub>	CuK $\alpha$ radiation
$M_r = 674.72$	$\lambda = 1.5406 \text{ \AA}$
Cubic	21 reflections
<i>Fm</i> 3 <i>m</i>	
$a = 11.122(3) \text{ \AA}$	$2\theta = 3^\circ\text{--}100^\circ$
$V = 1375.927(4) \text{ \AA}^3$	$T = 296 \text{ K}$
$Z = 4$	
$D_x = 3.25 \text{ g/cm}^3$	
$D_m = 3.07 \text{ g/cm}^3$	
Data collection	
Siemens D-5000 diffractometer	$h = 0 \rightarrow 4$
$\omega/2\theta$ scans	$k = 0 \rightarrow 5$
	$l = 0 \rightarrow 8$
Absorption correction:	
Empirical	
$T_{\min} = 0.55, T_{\max} = 0.85$	
Intensity variation: < 1%	

**TABLE 4B**  
Crystallographic and Experimental Details for Cs<sub>2</sub>KEuCl<sub>6</sub>

Cs <sub>2</sub> KEuCl <sub>6</sub>	CuK $\alpha$ radiation
$M_r = 669.585$	$\lambda = 1.5406 \text{ \AA}$
Cubic	17 reflections
<i>Fm</i> 3 <i>m</i>	
$a = 11.163(3) \text{ \AA}$	$2\theta = 3^\circ\text{--}100^\circ$
$V = 1391.063(4) \text{ \AA}^3$	$T = 296 \text{ K}$
$Z = 4$	
$D_x = 3.19 \text{ g/cm}^3$	
$D_m = 3.12 \text{ g/cm}^3$	
Data collection	
Siemens D-5000 diffractometer	$h = 0 \rightarrow 4$
$\omega/2\theta$ scans	$k = 0 \rightarrow 5$
	$l = 0 \rightarrow 8$
Absorption correction:	
Empirical	
$T_{\min} = 0.55, T_{\max} = 0.85$	
Intensity variation: < 1%	

the important distance and angle values for the octahedral KCl<sub>6</sub>, TbCl<sub>6</sub>, and the dodecahedral cesium site. Figure 3 shows the unit cells of the terbium compound; this is very similar to the structure of the europium compound. Tables 4A and 4B give the experimental data of crystallographic study of Cs<sub>2</sub>KEuCl<sub>6</sub> and Cs<sub>2</sub>TbCl<sub>6</sub>. Thermogravimetric analyses show the start of the decomposition of both compounds above 500°C and the differential scanning calorimetry studies show that there is no melting point transition.

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