Phase-Transition Variation with Composition in Solid Solutions of $K_2Cd_2(SO_4)_3$ with $TlzCd_2(SO_4)_3$

BY A. SUTERA,* K. NASSAU AND S. C. ABRAHAMS
Bell Laboratories, Murray Hill, New Jersey 07974, USA

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Abstract
Polycrystalline samples of $(K_xTlz_{1-x})_2Cd_2(SO_4)_3$ have been prepared with $x = 0[0-125]1.0$. The phase transition temperature, liquidus and solidus temperatures, lattice parameters and unit-cell volume at 298 K have been determined for each composition. The phase transition temperature varies linearly with $x$ for $0.125 < x < 1.0$, and the solidus curve varies linearly with $x$ over the entire range. Mixed crystals are cubic at 298 K for $x \leq 0.645$ and are orthorhombic at higher values of $x$. The cubic lattice parameter varies linearly with $x$ for $0.125 < x < 0.645$, the lengths of the orthorhombic $a$, $b$ and $c$ axes vary linearly with $x$ for $0.645 < x < 1.0$, and the unit-cell volume varies linearly with $x$ for $0.125 < x \leq 1.0$.

Introduction
Ferroelastic $K_2Cd_2(SO_4)_3$ undergoes a phase transition at $T_c = 432$ K from orthorhombic symmetry, point group 222, to the paraelastic cubic phase with point group $23$ (Abrahams, Lissalde & Bernstein, 1978). Cubic $K_2Cd_2(SO_4)_3$ is isostructural with the mineral langbeinite, $K_2Mg_2(SO_4)_3$ (Zemann & Zemann, 1957). Phase transitions have been observed in a number of langbeinite-type structures with formula $A_2B_2(SO_4)_3$, where $A = NH_4$, $K$, $Rb$, $Cs$, $Tlz$; $B = Mg$, $Ca$, $Mn$, $Fe$, $Co$, $Ni$, $Cd$. Isostructural $TlzCd_2(SO_4)_3$ is cubic above 130 K (Brezina & Glogarović, 1972). It was of interest to prepare mixed crystals of $K_2Cd_2(SO_4)_3$ $- TlzCd_2(SO_4)_3$ in order to study the variation of the ferroelastic–paraelastic phase transition temperature with composition in this system. A composition with phase transition temperature close to ambient would have potentially useful properties.

Experimental
Polycrystalline samples of $(K_xTlz_{1-x})_2Cd_2(SO_4)_3$, with $x = 0[0-125]1.0$, were prepared from reagent grade (purity greater than 99.6%) sulfates that were previously dried at 440 K. The mixed sulfates were allowed to react at 875 K for a period of two weeks, with daily grinding to enhance their homogeneity. Single-phase powder patterns were generally obtained within ten days. Limited attempts at growing single crystals of intermediate composition, with $0 < x < 1.0$, from aqueous solution did not give usable material.

Lattice parameters for the cubic phase were measured at room temperature from tracings taken with a Rigaku Miniflex diffractometer, with Ni-filtered Cu radiation ($\lambda = 1.5406 \text{ Å}$). The orthorhombic lattice parameters were derived from measurements taken from powder patterns recorded in an IRDAB XDC700 Guinier focusing camera, with Cu $K_\alpha$ radiation ($\lambda = 1.540598 \text{ Å}$) with $x-Al_2O_3$ ($a = 4.75802, c = 12.99084 \text{ Å}$) as the internal standard. Refinement of lattice parameters from the measured $d$ spacings was made with the method of least squares. Intensity calculations, based on the structure of $K_2Cd_2(SO_4)_3$ at room temperature (Abrahams & Bernstein, 1977), were required to index the overlapping lines of the orthorhombic patterns.

The orthorhombic cubic phase transition temperatures, and the melting endotherms, were measured by differential thermal analysis (DTA) in a DuPont 990 thermal analyzer. A heating rate of 10 K min$^{-1}$ was used for the transition temperature data and 20 K min$^{-1}$ in flowing nitrogen for the melting data. Based on the reproducibility of the line widths and experience with a range of known transitions, the standard deviation in the transition temperature data is estimated as 3 K, that in the melting data as 5 K.

* Summer Research Program Student. Present address: Vassar College, Poughkeepsie, New York 12601, USA.

Fig. 1. Variation of $T_c$ with $x$ in the mixed crystal $(K_xTlz_{1-x})_2Cd_2(SO_4)_3$ is indicated by solid circles. Variation of the liquidus and solidus temperatures is indicated by open circles and open squares respectively, with temperature scale as given at the right side.
Variation of \( T_p \) and melting point with composition

The experimental values of \( T_p \) are found to vary linearly with \( x \) for all compositions of \((K_x\text{Tl}_{1-x})_2\text{Cd}_2(\text{SO}_4)_3\) except \( x = 0 \) as seen in Fig. 1. For \( T_p = 300 \) K, \( x \) is 0.645. Values of \( T_p \) for \( x = 0 \) and 1.0 were obtained on single crystals grown by the methods of Březina & Havránková (1974) and Nassau & Shiever (1977), respectively.

The liquidus and solidus curves are shown in Fig. 1. Melting is congruent only at \( x = 1 \). At other values, two or more distinct endotherms are observed in the DTA, often with overlap; the highest and lowest endotherm temperatures only are given for each value of \( x \) in Fig. 1. This figure represents an arbitrary section through a multicomponent system and therefore is not required to be a true binary nor even a pseudo-binary phase diagram. Indeed, the binary phase rule does not apply as may be seen for example, by the continuous slope of the lowest endotherm curve.

Variation of lattice parameters and volume with composition

The variation of \( x \) with cubic lattice parameter at room temperature is linear for compositions with \( 0.125 < x \leq 0.625 \), as shown in Fig. 2. The room-temperature orthorhombic phase at \( x = 0.68 \) was transformed into the cubic phase by heating to 320 K in a stream of warm air, with lattice parameter as in Fig. 2. The value for \( x = 0 \) is taken from Swanson, McMurdie, Morris & Evans (1970) and is in complete agreement with our value of 10.384 (1) Å. For compositions at room temperature with \( 0.68 < x \leq 1.0 \), each of the orthorhombic lattice parameters varies linearly with \( x \). Resolution difficulties precluded measurements closer to \( x = 0.645 \), the room-temperature boundary between the orthorhombic and cubic phases. The lattice constants at \( x = 1.0 \) are taken from Abrahams & Bernstein (1977).

The variation of lattice constants with temperature for \( x = 1.0 \) (Lissalde, Abrahams, Bernstein & Nassau, 1979) closely resembles the compositional variation shown in Fig. 2, the lattice parameters reverting sharply from the orthorhombic values to the cubic value in a temperature interval less than 5 K.

The unit-cell volume varies linearly with \( x \) for \( 0.125 \leq x \leq 1.0 \), as seen in Fig. 3. Unlike the sharp change in unit-cell volume variation with temperature found at the phase transition for the composition \( x = 1.0 \) (Lissalde et al., 1979), the phase change that occurs at room temperature for \( x = 0.645 \) has no significant influence on the volume.

Replacement of K by \( \text{Tl} \) in \((K_x\text{Tl}_{1-x})_2\text{Cd}_2(\text{SO}_4)_3\)

Two independent K sites have been determined for the composition \( x = 1.0 \) (Abrahams & Bernstein, 1977). One is eight coordinated, the other ten coordinated, for \( \text{K} – \text{O} \) contacts less than 3.25 Å. The effective ionic radius of \( \text{Tl}^+ \) is about 0.08 Å greater than that of \( \text{K}^+ \) for both coordinations (Shannon, 1976). The distribution of \( \text{Tl} \) between the two available sites for compositions with \( x < 1.0 \) is probably but not necessarily equal for all values of \( x \). The departures from a linear dependence on composition, shown in Figs. 1, 2 and 3, at \( 0 \leq x \leq 0.125 \) suggest that the distribution of \( \text{Tl}^+ \) and \( \text{K}^+ \) in this range is not equal over the two sites. It is known (Abrahams et al., 1978) that the \( \text{K}^+ \) ions move less than 0.05 Å in the temperature range 298–417 K, for \( x = 1.0 \), with displacements averaging 0.16 Å between 417.5 K and \( T_p = 432 \) K. These motions are related to the rotations of the \( \text{SO}_4^- \) ions as the phase transition is approached and completed. An investigation of the atomic distribution at the monovalent atom sites for \( x < 0.125 \) would be necessary in order to clarify the cause of the nonlinearities observed in this region.

Fig. 2. Variation of the cubic lattice parameter a with composition x in \((K_x\text{Tl}_{1-x})_2\text{Cd}_2(\text{SO}_4)_3\) at room temperature is indicated by closed circles, the orthorhombic a axis by open circles, the b axis by open squares, the c axis by open diamonds. The closed circle at \( x = 0.68 \) represents the cubic a axis of a sample measured at 320 K. Error bars represent ±1 e.s.d. The vertical line at \( x = 0.645 \) represents the boundary between cubic and orthorhombic phases at 300 K.

Fig. 3. Variation of the unit-cell volume of \((K_x\text{Tl}_{1-x})_2\text{Cd}_2(\text{SO}_4)_3\) with x at room temperature. Error bars represent ±1 e.s.d. End-member values are from single-crystal lattice-constant measurements (see text).
It may be noted that the cubic lattice parameter in solid solutions of composition \([(NH_4)_xTl_{1-x}]_2(SO_4)_3\] shows a strong negative deviation from linearity (i.e. from Vegard's law) over the range \(0 \leq x \leq 1.0\) (Ikeda & Saeki, 1977), in contrast to the strict linearity observed in the present study.

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References