Phase Transition at 555 K in Nonlinear Optic Pb₅Cr₃F₁₉

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Abstract

The a lattice constant of tetragonal Pb₅Cr₃F₁₉, 14.384(5) Å at 295 K, expands sharply by 0.6% on heating through the Curie temperature [Tc = 555(5) K] as the c lattice constant, 7.408(2) Å at 295 K, abruptly contracts by 0.6% and the uniaxial indicatrix of the crystal reverses sign from negative to positive. The phase transition is first order. The a lattice constant below Tc fits a second-order polynomial of the form \( a(T) = a(295) [1 + a_1(T - 295) + a_2(T - 295)^2] \) with \( a_1 = 1.2 \times 10^{-6} \) K⁻¹ and \( a_2 = 9.8 \times 10^{-8} \) K⁻²; the c lattice constant thermal variation is linear with \( c(T) = c(295) + 10.3 \times 10^{-6} (T - 295) \) K⁻¹. Above Tc, the thermal expansion of both axes becomes linear with \( a(T) = a(555) + 2.5 \times 10^{-6} (T - 555) \) K⁻¹ and \( c(T) = c(555) + 4.9 \times 10^{-6} (T - 555) \) K⁻¹, for \( a(555) = 14.568(8) \) Å and \( c(555) = 7.388(5) \) Å. The birefringence at 295 K is \( 310 \times 10^{-4} \) and at 640 K is \( -35 \times 10^{-4} \), for \( \lambda = 543 \) nm. The entropy change at Tc is \( 13(3) \) J mol⁻¹ K⁻¹.

Introduction

Study of the crystal chemistry of many \( MF_2-7F_3 \) systems, where \( M \) is Sr, Ba or Pb and \( T \) is Al, Sc, Ti, V, Cr, Fe, Co, Ga or In, reveals a large family of tetragonal phases with structures related to that of the archetypes SrAlF₅ or Sr₃(FeF₆)₂. Each archetype possesses the attributes of ferroelectricity, undergoing a phase transition to the paraelectric phase at the Curie temperature (Abrahams, Ravez, Simon & Chaminade, 1981; Abrahams, Ravez, Canouet, Granenc & Loiacono, 1984). A phase transition at 550 K with entropy change of \( 17(2) \) J mol⁻¹ K⁻¹ has been reported in Pb₅(CrF₆)₂ on the basis of a calorimetric and dielectric permittivity study (Abrahams et al., 1984). The present paper reports the thermal dependence of the unit-cell dimensions and uniaxial indicatrix in this crystal between 295 and 610 K. Accurate density measurement shows that the stoichiometric composition is given by the formula Pb₅(CrF₆)₂, not Pb₅(CrF₆)₁₂. It may be noted that the fluoride mixture 3PbF₂ + 2CrF₃ required in preparing the latter material contains 60-0% PbF₂, whereas the former composition as prepared from 5PbF₂ + 3CrF₃ contains 62-5% PbF₂.

Preparation and crystal growth

Polycrystalline Pb₅Cr₃F₁₉ is produced by the reaction of 5PbF₂ with 3CrF₃ in a gold tube sealed under dry argon, on heating to 775 K for 15 h. The starting materials were 99-95% pure, from commercial sources. Single crystals have been grown by Chaminade (1985); he used the Bridgman method, with the stoichiometric mixture sealed in a Pt tube under dry helium. The temperature is raised to 30 K above the melting point \( (T_m = 955) \) K and the crucible is passed at a rate of \( 1 \) mm h⁻¹ through a temperature gradient of \( 40 \) K cm⁻¹. The resulting crystals form square prisms, elongated along the [001] growth direction. The maximum dimensions of the transparent deep green crystals are \( 2.0 \times 0.5 \times 0.5 \) mm.

Density and composition

The density measured by immersion in bromobenzene \( (d_{295} = 1.4966 \) g cm⁻³) is \( 6.67(5) \) g cm⁻³. For the composition Pb₅Cr₃F₁₉, with \( a = 14.384(5) \) Å and \( c = 7.408(2) \) Å, the density is \( 6.729 \) g cm⁻³ whereas the composition Pb₃Cr₂F₁₂ corresponds to \( D_{calc} = 6.198 \) g cm⁻³. The correct composition is hence Pb₅Cr₃F₁₉, in agreement with that recently determined for Pb₅W₃O₉F₁₀ (Marsh, Abrahams & Ravez, 1985). The second-order nonlinear dielectric susceptibility of Pb₅Cr₃F₁₉ may thus be taken as \( 0.005(1) \times 10^{-1} \) V⁻¹ m⁻¹ (Abrahams et al., 1984).

Unit-cell thermal dependence and expansion coefficients

The lattice constants of the tetragonal unit cell were measured at 295, 380, 450, 500, 540, 550, 555, 565, 575 and 610 K on polycrystalline material in a Guinier–Simon Enraf–Nonius camera model FR 553; see Fig. 1. The radiation used was Cu Kα₁ with...
\[ \lambda = 1.54051 \, \text{Å} \] and measurements were in the range \( 5 < \theta < 40^\circ \). The thermal dependence of the \( a \) lattice constant may be fitted by linear regression to a second-order polynomial of the form \( a^2 = a^2_{05} [1 + \alpha_1 AT + \beta_1 (AT)^2] \), corresponding to the curve shown in Fig. 1, with \( \alpha_1 = 1.2 \times 10^{-6} \, \text{K}^{-1} \) and \( \beta_1 = 9.8 \times 10^{-8} \, \text{K}^{-2} \); the \( c \) lattice constant varies linearly with temperature and has thermal expansion coefficient \( \alpha_3 = 10.3 \times 10^{-6} \, \text{K}^{-1} \). The volume expansion is fitted by a second-order polynomial with coefficients \(-0.93 \times 10^{-6} \, \text{K}^{-1} \) and \( 28.9 \times 10^{-9} \, \text{K}^{-2} \); a linear fit to either the \( a \) lattice constant or unit-cell volume thermal dependence results in deviates larger than expected for a normal distribution.

The unit-cell thermal expansion is very small and linear above the phase transition, with \( \alpha_1 = 2.5 \) and \( \alpha_3 = 4.9 \times 10^{-6} \, \text{K}^{-1} \). All thermal-expansion-coefficient e.s.d.'s are about 25% of the coefficient value. The sharp discontinuity in both lattice constants, 0.58% for \( a \) and -0.57% for \( c \), is also apparent in the 0.58% volume expansion at \( T_C \). The high- and low-temperature phases of Pb\(_5\)Cr\(_3\)F\(_19\) are found to coexist in the range \( T_C \pm 5 \, \text{K} \). In this thermal regime, the diffraction linewidths increase very significantly. It is of interest to note that the ratio \( c/a \) decreases from 0.5150 at 295 K to 0.5128 at 550 K, with a further sharp decrease to 0.5071 at the phase transition.

### Birefringence thermal dependence

Optical measurements were made using a hot-stage Leitz Ortholux II Pol polarizing microscope, with the single crystal maintained under dry nitrogen. The resulting thermal dependence of \( \Delta n = n_0 - n_f \) for \( \lambda = 543 \, \text{nm} \), presented in Fig. 2, shows a hysteresis of about 48 K at the phase transition. Both high- and low-temperature phases are observed in the microscope to coexist at \( T_C \), as is also found in the X-ray diffraction measurements. Single crystals characteristically develop, within 5 K of the phase transition, a sharply defined and mobile domain boundary that separates the two phases. The change in optic sign of Pb\(_5\)Cr\(_3\)F\(_19\) from negative to positive suggests that the crystal becomes instantaneously isotropic at \( T_C \) as \( \Delta n = 0 \) and the \( c/a \) ratio approaches 1/2.

### Characterization of Pb\(_5\)Cr\(_3\)F\(_19\) phase transition

The discontinuities observed in unit-cell dimensions, see Fig. 1, together with the coexistence of both low- (pyroelectric, point group 4) and high- (paraelectric,
point group $4/m$) temperature phases at the Curie temperature observed both in the X-ray diffraction and optical studies, are strongly indicative of a first-order phase transition. Differential thermal analyses, made using a Trifux model calorimeter (Thermanalyse SA) with a 190 mg sample and a heating (cooling) rate of $1.3 \ \text{K min}^{-1}$, gave a transition temperature of 563.9 K on heating and 535.8 K on cooling, for an average $T_c$ of 549.9 K. The average entropy change ($\Delta S$) associated with the phase transition is $13(3) \ \text{J mol}^{-1} \ \text{K}^{-1}$. Both $T_c$ and $\Delta S$ are in good agreement with the previous values reported for the composition Pb$_3$Cr$_2$F$_{12}$ (Abrahams et al., 1984). The atomic arrangement in Pb$_3$Cr$_3$F$_{19}$ has not yet been determined, but is anticipated to be similar to that in isostructural Pb$_3$W$_3$O$_9$F$_{10}$ (Marsh et al., 1985; Arquis-Canouet, Ravez, Chaminade, Hagenmuller, Abrahams & Marsh, 1986).

The low-temperature phase is expected to exhibit ferroelectric behavior. Examination of the relationships between atomic arrangement and the experimental observations reported in this communication is deferred until the crystal structure determination is complete.

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References


