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Thermal properties of the pyrochlore, $Y_2Ti_2O_7$

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ABSTRACT

The thermal conductivity and heat capacity of high-purity single crystals of yttrium titanate, $Y_2Ti_2O_7$, have been determined over the temperature range $2\,K \leqslant T \leqslant 300\,K$. The experimental heat capacity is in very good agreement with an analysis based on three acoustic modes per unit cell (with the Debye characteristic temperature, θ_D, of ca. 970 K) and an assignment of the remaining 63 optic modes, as well as a correction for $C_p - C_v$. From the integrated heat capacity data, the enthalpy and entropy relative to absolute zero, are, respectively, $H(T = 298.15\,K) - H_0 = 34.69\,kJ\,mol^{-1}$ and $S(T = 298.15\,K) - S_0 = 211.2\,J\,K^{-1}\,mol^{-1}$. The thermal conductivity shows a peak at ca. $\theta_D/50$, characteristic of a highly purified crystal in which the phonon mean free path is about 10 μm in the defect/boundary low-temperature limit. The room-temperature thermal conductivity of $Y_2Ti_2O_7$ is $2.8\,W\,m^{-1}\,K^{-1}$, close to the calculated theoretical thermal conductivity, κ_{min}, for fully coupled phonons at high temperatures.

1. Introduction

Yttrium titanate, $Y_2Ti_2O_7$, belongs to the family of compounds with the general chemical formula $A_2B_2O_7$, isostructural to the mineral pyrochlore, (NaCa)(NbTa)O_6F/(OH) [1]. Pyrochlores are refractory materials with important properties, including ionic conductivity [2,3], optical nonlinearity [4] and high radiation tolerance [5]. They have many potential applications, including thermal barrier coatings [6], high-permittivity dielectrics [7], solid electrolytes in solid-oxide fuel cells [8], and materials for safe disposal of actinide-containing nuclear waste [9]. Furthermore, pyrochlores have promise as ceramic pigments, given their high melting points (~1600 °C), high refractive index ($n > 2$), and the ability to accept transition metal dopants [10]. The general pyrochlore structure has high symmetry (*Fd*-3*m*) and is constituted of vertex-sharing tetrahedra as shown schematically in Fig. 1.

Given the interesting properties of pyrochlores, it is not surprising that their fundamental thermal properties also have attracted attention. Studies include molecular dynamics simulations of the thermal conductivities of a large number of pyrochlores [11], theoretical investigations of structure and thermal conductivity of $La_2Zr_2O_7$ [12] and experimental determinations of formation enthalpies of titanate pyrochlores [13].

Yttrium titanate, $Y_2Ti_2O_7$, often abbreviated as YTO, is an especially important member of the pyrochlore family. It has both extremely strong electron–phonon interactions and high oxygen vacancy concentrations (the large unit cell [$Z = 8$] of YTO allows some of the oxygen ions to move relatively freely) resulting in low diffusion activation energy [14]. Due to the large number of oxygen vacancies, it can be an n-type semiconductor via doping of the Y^{3+} and Ti^{4+} sites [15] and an increase in conductivity of up to two orders of magnitude can occur on doping [16]. The fact that $Y_2Ti_2O_7$ is diamagnetic makes it one of the most amenable pyrochlores for detailed examination, especially by NMR [15]. As the first reported pyrochlore to split water into H_2 and O_2 under UV irradiation, $Y_2Ti_2O_7$ with excess Y has potential as a photocatalyst [17]. $Y_2Ti_2O_7$ also shows promise as a buffer layer on superconductor substrates [18]. A recent theoretical study of the structure and bonding properties of $Y_2Ti_2O_7$ has shown it to be a good candidate for a hard material due to short inter-atomic distances between ions causing the Ti–O and Y–O bonds to have covalent character [19].

Considering the interest in pyrochlores, and the special importance of $Y_2Ti_2O_7$, we have selected this pyrochlore for a detailed experimental investigation of thermal properties. In the present work, the thermal conductivity and heat capacity of $Y_2Ti_2O_7$ have been determined over a wide temperature range (2–300 K), and the contributions of the various degrees of freedom

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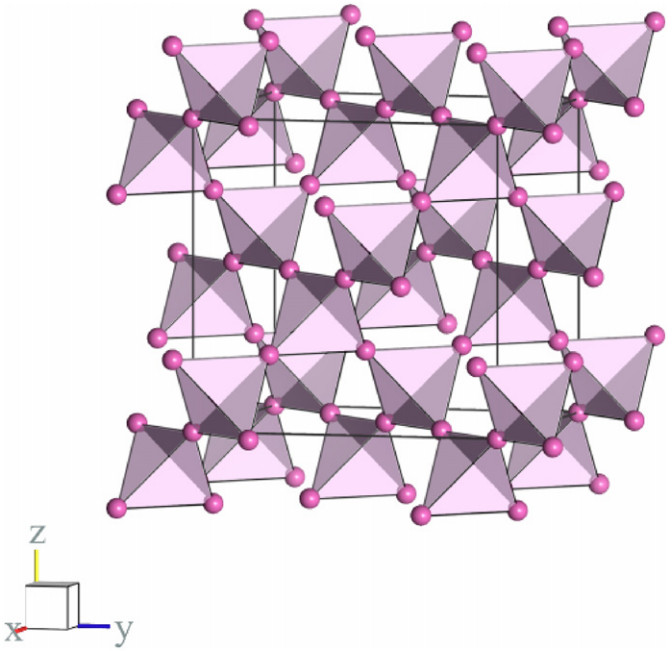

Fig. 1. A general view of the pyrochlore structure, showing the linked polyhedra.

to the latter have been assessed. The concomitant advanced understanding concerning the lattice dynamics of $Y_2Ti_2O_7$ provides a firm foundation for analysis of the temperature-dependence of its thermal conductivity and comparison with other pyrochlores.

2. Experimental materials and methods

2.1. Preparation of $Y_2Ti_2O_7$

Several large single crystals of $Y_2Ti_2O_7$ were grown using a two-mirror NEC floating zone image furnace. The details of the crystal growths were similar to those previously reported for single crystal $Tb_2Ti_2O_7$ [20]. The starting materials for the polycrystalline rods were 99.999% pure Y_2O_3 and 99.995% pure TiO_2, both from Alfa Aesar. These materials were pre-annealed at 1273 K, and the resulting rod of $Y_2Ti_2O_7$ was sintered at 1473 K. The final single crystal growth speed in the image furnace was 5 mm h^{-1} and the growth was carried out in air. Smaller single crystals, used for the thermal measurements, were cut from the larger crystals. $Y_2Ti_2O_7$ is cubic and the samples were not oriented.

2.2. Thermal measurements

Thermal conductivities (κ) over the temperature range from 2 to 300 K were determined using the thermal transport option of a Physical Property Measurement System (PPMS, by Quantum Design). A two-probe configuration (heater and hot thermometer on one lead; cold foot and cold thermometer on the other) was used and the determination of κ was based on steady-state thermal gradients [21]. A piece of a single crystal of mass 16.77 mg (cross-sectional area: 4.51 mm^2; thickness 0.74 mm), polished on both faces, was epoxied (Tra-Duc 2902 from Tra-Con, Inc.) to two disk-shaped gold-plated copper leads. The temperature drop across the sample during measurements was typically $\Delta T \sim 0.03\,T$. Thermal conductivity was measured using step-wise methods. The maximum heater power was 50 mW. Uncertainty in thermal conductivity measurements is within 5%.

Experimental heat capacities of several pieces of single crystals of $Y_2Ti_2O_7$ cut from larger single crystals and polished on at least one side (for good thermal contact with the tray) were measured over the temperature range from 2 to 300 K using the relaxation calorimetric technique of the PPMS. Four single crystals of various masses (9.93, 16.77 [same sample as for thermal conductivity], 21.10 and 31.65 mg) were measured. In principle, larger samples should give more accurate heat capacity measurements because of their larger contribution to the total heat capacity, but we have found that sometimes large samples give falsely low heat capacity measurements in the PPMS due to long relaxation times [22], so measurement of a range of sample masses is recommended for high accuracy. For $T > 20$ K, these samples contributed in the following proportions to the total heat capacity: from 35% to 55% (9.93 mg sample), or from 65% to 80% (31.65 mg sample). The two-tau method of heat capacity data analysis [23], which allows separately for relaxation of the temperature within the sample and within the addenda, was used. Overall uncertainty in the heat capacity is within 1% in the range 5 K $< T <$ 300 K, and within 5% for $T < 5$ K [22].

3. Results and discussion

3.1. Heat capacity of $Y_2Ti_2O_7$

Since the heat capacity provides direct information concerning the lattice dynamics, which is important to the interpretation of the thermal conductivity results, we begin with discussion of the heat capacity results.

The heat capacity of $Y_2Ti_2O_7$ (Fig. 2; full data tables given in the Supplementary Information) is smooth and shows no evidence of phase transitions over the temperature range examined. Furthermore, the data showed no dependence on the sample mass for $T < 70$ K, but at higher temperatures the apparent heat capacity of the most massive sample fell below the other results, indicating inaccuracy due to a thermal lag in the sample during the measurement. In further analysis and discussion presented below, the data for the 31.65 mg sample for $T > 70$ K are omitted.

The low-temperature ($T < 30$ K) heat capacity of a polycrystalline sample of $Y_2Ti_2O_7$ has been reported recently [24] and is in good agreement with the present data in the temperature range of overlap. One advantage of the wider temperature range here is further quantification of the chemical thermodynamics of

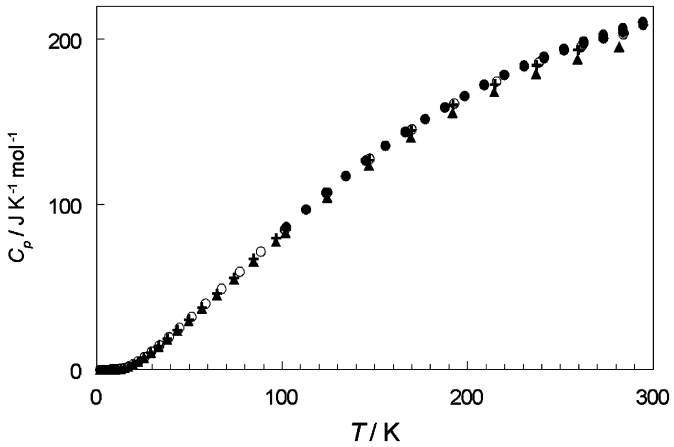

Fig. 2. Heat capacity of $Y_2Ti_2O_7$ as a function of temperature. Sample mass: +, 9.93 mg; ●, 16.7 mg; ◦, 21.10 mg and ▲, 31.65 mg.