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Low-temperature heat capacities of Y_2GaSbO_7 and R_2FeSbO_7 (R = Y, Dy) pyrochlore compounds: Quasi-harmonic phonons calculation

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ABSTRACT

Heat capacities at constant pressure, $C^{\circ}_{p,m}$, of three polycrystalline pyrochlore compounds, Y_2GaSbO_7, Y_2FeSbO_7 and Dy_2FeSbO_7, have been measured in the temperature range up to 300 K. Temperature variation of the Debye temperatures, $\theta_D(T)$, for Y_2GaSbO_7 is determined using a quasi-harmonic expression of Debye lattice heat capacity, which has been employed to estimate the phonon heat capacity, C_{ph}, for the other two compounds, e.g., Y_2FeSbO_7 and Dy_2FeSbO_7. Theoretical analysis using phonon model shows that the acoustic and optic phonons contribute significantly to the thermodynamic properties. The effect of anharmonicity in the lattice vibrations at higher temperature (above 220 K) was also considered for Y_2GaSbO_7. The C_{ph} of Y_2FeSbO_7, calculated using the experimental infra-red and Raman phonon spectra, are in good agreement with the measured heat capacity data and thus provides a good taste of understanding to the molecular dynamics in the pyrochlore structure. The Schottky heat capacity has been deduced from the crystal-field level scheme of Dy^{3+} ions and added to the C_{ph} of Dy_2FeSbO_7 to estimate the total heat capacity, which is in reasonable agreement with the experimental heat capacity, $C^{\circ}_{p,m}$, of Dy_2FeSbO_7. From the integrated heat capacity data, the entropy and enthalpy relative to absolute zero have been generated for Y_2GaSbO_7 and Y_2FeSbO_7. The room-temperature thermal conductivity was estimated to be $\sim 2\ W \cdot m^{-1} \cdot K^{-1}$ for Y_2GaSbO_7 implying that Y_2GaSbO_7 could be a potential candidate for thermal barrier coating material.

1. Introduction

The title materials, Y_2GaSbO_7, Y_2FeSbO_7 and Dy_2FeSbO_7, belong to the family of pyrochlore oxides with the chemical formula $R_2M'M''O_7$, or more general $R_2M_2O_7$, which have gained considerable research interest in basic science, materials science and engineering in recent times, owing to their highly scientific and technological importance for multifunctional properties. During the last few decades, the pyrochlore compounds have found many potential technological applications [1], including thermal barrier coatings used in high combustion engines [2–5], solid electrolytes in solid-oxide fuel cells [6–8], safe disposal of nuclear waste [9,10], etc. Knowledge of the thermodynamic properties, e.g., heat capacity, entropy, enthalpy, thermal conductivity, thermal expansion, etc., of these compounds is precisely required for all industrial applications in order to determine their durability under typical process conditions. Until now only few thermodynamic studies have been reported for the pyrochlore compounds, e.g. $R_2Zr_2O_7$ (R^{3+} = La, Nd, Gd, Eu) [4,5,7,9,11–14], $R_2Hf_2O_7$ [15], $R_2Ti_2O_7$ [8,10,16] in the temperature ranging from $T = 2$ K to 1700 K for these compounds.

The thermal properties of materials are strongly influenced by quantum effects at low temperatures, and by statistical distributions of ions over different electronic levels and also by the lattice dynamics at moderate and higher temperatures. Heat capacity provides an important probe to study these thermodynamic effects. For insulating, non-magnetic crystalline compounds, the heat capacity, called 'phonon heat capacity' (C_{ph}), is caused by the acoustic and optic branches of lattice vibrations, which tends to zero as $T \rightarrow 0$ and can be demonstrated by the Debye or Einstein model of lattice heat capacity. There is another important contribution to the heat capacity, called electronic Schottky heat capacity (C_{Sch}), which is required for the statistical (thermal) distributions of paramagnetic ions over the $(2J + 1)$ quantum levels of degenerate ground J-multiplet, split by the surrounding crystal-field (CF) at the site of paramagnetic ions. In magnetic solids containing rare-earth or transition metal ions, the heat capacity contribution, C_{mag}, due to magnetic ordering of ions is superimposed on the phonon C_{ph} characteristics and shows a peak at the ordering

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temperature. Since the pyrochlores, R_2FeSbO_7, contain $4f^n$ rare-earth (R^{3+}) and $3d^5$ iron (Fe^{3+}) magnetic ions, they are expected to be the ideal compounds to investigate the different contributions of heat capacity.

We have recently reported heat capacity of the three pyrochlore powder compounds, Dy_2FeSbO_7 (DF), Y_2FeSbO_7 (YF) and Y_2GaSbO_7 (YG), in the temperature range of $T = 2\text{–}45$ K with and without magnetic field [17]. The DF appears to have disordered spin-ice-like low temperature state with the magnetic entropy value of $\Delta S_{mag} \approx 4.61$ $J \cdot mol^{-1} \cdot K^{-1}$, which is slightly larger than the expected for a spin-ice system. The excess entropy (~ 0.5 $J \cdot mol^{-1} \cdot K^{-1}$) is contributed by the ferromagnetic ordering of Fe^{3+} spins observed at ~ 11 K for DF and YF samples. The YG is a diamagnetic, insulating compound, and therefore, plays an important role in estimating the phonon C_{ph} contribution to the heat capacity of DF and YF samples. The heat capacity of YG follows a Debye law, $C_{ph} = \alpha T^3 + \beta T^5$ below $T \sim 26$ K, and above this range the low-temperature phonon contribution increases over the measured heat capacity data, since the Debye temperature (θ_D) is a complex function of T/K at higher temperature. The θ_D value of YG was scaled to determine the C_{ph} of DF and YF at low temperatures, which was subtracted off the measured heat capacity to obtain the C_{mag} of DF and YF below 20 K [17].

The aim of the present paper is to extend our work with low temperature measurements of heat capacity, $C^\circ_{p,m}$, at constant pressure in the temperature range up to 300 K and to calculate the temperature dependence of the Debye temperature, $\theta_D(T)$, of these samples, which will be converted back to estimate the phonon heat capacity, C_{ph}, using quasi-harmonic expression of Debye lattice heat capacity for these samples in the experimental temperature range. The effects of anharmonicity in the lattice vibrations at high temperature should also be considered. The C_{ph} of YF may also be calculated using the observed Fourier-transform infra-red (FT-IR) and Raman phonon spectra [18] within the framework of Debye and Einstein models. The 'spectroscopic' Schottky heat capacity of DF has been deduced from the crystal-field level scheme of Dy^{3+} ions in DF and added to the C_{ph} of DF to estimate and compare with the experimental heat capacity.

2. Experimental

2.1. Sample preparation and characterization

Polycrystalline samples of R_2FeSbO_7 (R = Y, Dy) were synthesized from stoichiometric mixtures of R_2O_3, Fe_2O_3, and Sb_2O_3 powders by conventional solid-state reaction route. Detailed preparation method, characterization by X-ray powder diffraction (XRD) and its Rietveld analysis, were already described elsewhere [19]. The XRD profiles of YF and DF samples are included in the supplementary file (Fig. S1).

Y_2GaSbO_7 (YG) powder was prepared by conventional solid-state reaction approach using powders of Y_2O_3, Ga_2O_3 and Sb_2O_5. All powders were preheated to 200 °C for 4 h to remove moistures. Stoichiometric mixtures were intimately mixed and hand ground in an agate mortar for 10 h, and subsequently put into an alumina crucible for calcination at 1320 °C in air for 44 h with intermittent regrinding and pelletizing. Finally white powder sample was obtained.

The XRD at room temperature were recorded to identify the crystalline phase of the sintered powder sample using CuKα radiation ($\lambda = 0.15418$ nm) by a Rigaku Miniflex 600 bench-top powder diffractometer operating at 40 kV and 15 mA. The powder diffraction diagrams were obtained by scanning with a speed of 4°/min over a range of $2\theta = 10°\text{–}90°$ at 0.02° step-intervals. The XRD profile pattern were analyzed by Rietveld method using a Fullprof software introducing the atomic information setting the origin at R-site and taking account of the space group of the pyrochlore structure model $Fd3m$. The refinement results indicated a good agreement between the observed and calculated Bragg's intensities of Y_2GaSbO_7 (Fig. 1) for the pyrochlore-type structure, confirming no trace of any impurity. The detailed structural analysis for Y_2GaSbO_7 sample was reported in Ref. [17].

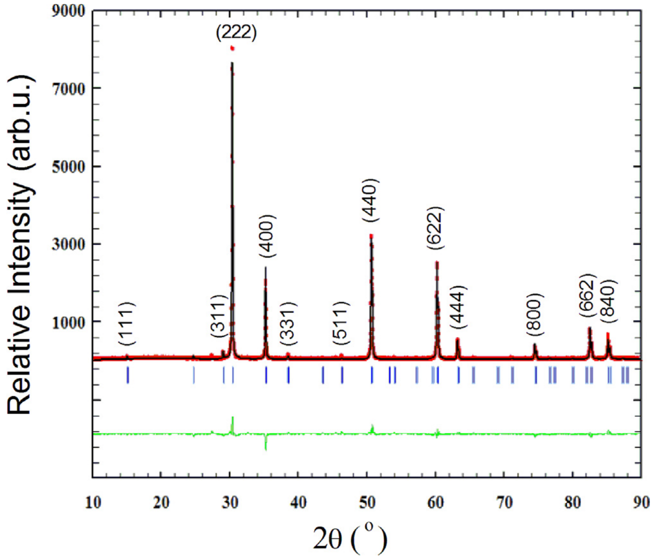

Fig. 1. XRD profile of Y_2GaSbO_7: observed (red points), calculated (solid lines), and the difference (green lines). Vertical marks (in blue) correspond to the allowed Bragg reflections for cubic space group $O_h^7 - Fd3m$. Most intense and significant (hkl) reflections are also denoted.

The phase purity, homogeneity, stoichiometry, atomic compositions, average particle size and surface morphology of the sintered compounds were investigated using the scanning electron microscope (SEM), manufactured by CARL ZEISS (Model: EVO LS10), equipped with energy dispersive X-ray analyzer (EDAX) from Oxford Instruments, with voltage of 20 kV. The samples for micro-structural and microanalysis determinations were deposited on a carbon tape and coated with a gold-palladium film using sputtering method.

The purity of the samples and the starting materials as well as the characterization methods are summarized in Table 1.

2.2. Heat capacity measurements

All three powder samples were pelletized for heat capacity measurements using polyvinyl alcohol (PVA) solution as binder with 8 ton pressure and heated to 1000 °C for 10 h for the complete removal of PVA. Low temperature heat capacity measurements at constant pressure $p \approx 9.2 \times 10^{-6}$ Torr = 1.2 mPa were performed by the thermal relaxation technique using the heat capacity attachment to the commercially available PPMS system (Quantum design) in the temperature range $T = (2.1\text{–}299)$ K. Measurement was carried out in different temperature ranges with different increments; for example, increment was programmed as 0.2 K at $T = (2.12\text{–}5)$ K, 0.4 K at $T = (5\text{–}16)$ K, 1 K at $T = (16\text{–}40)$ K, 2 K at $T = (40\text{–}80)$ K, and finally, 4 K at $T = (80\text{–}299)$ K for YG sample. Apiezon-N grease was used for thermal coupling of the pellet to the heat capacity attachment and the background signal for all the samples was, therefore, measured separately and subtracted. The uncertainties for the PPMS measurements of the standard molar heat capacities, $C^\circ_{p,m}$, for these samples were estimated at about ± 3% in the lowest range of temperatures $T = (2\text{–}10)$ K and