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Thermodynamic functions of magnesium gallate $MgGa_2O_4$ in the temperature range 0–1200 K

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ABSTRACT

The heat capacity of magnesium gallate $MgGa_2O_4$ was measured by adiabatic calorimetry (7–347 K) and differential scanning calorimetry (322–1200 K). Thermodynamic functions (heat capacity, entropy, enthalpy change and derived Gibbs energy) were calculated in the range 0–1200 K. Gibbs energy of formation of $MgGa_2O_4$ was estimated using the standard entropy $S^0(298.15\,K)$ from this work: $\Delta_f G^0(MgGa_2O_4, 298.15\,K) = -1594.3 \pm 4.3\,kJ\,mol^{-1}$. The Debye characteristic temperature $\Theta_D = 750 \pm 20$ K was calculated from heat capacity data and from elastic constants.

1. Introduction

Magnesium gallate $MgGa_2O_4$ has partially inverse spinel structure [1] and crystallizes in the cubic crystal system (space group $Fd\bar{3}m$, Z = 8).

$MgGa_2O_4$ is characterized by a very high melting point (about 1930 ± 10 C [1]) and exhibits relatively low chemical reactivity. The spinel-structured $MgGa_2O_4$ ceramics demonstrated excellent microwave dielectric properties which allow one to consider the magnesium gallate as a perspective compound that can be used for development of millimeter-wave devices such as filters, resonators and antennas [2].

Furthermore the thin film heterostructures for magnetoelectronic devices based on $MgGa_2O_4$ and $MgFe_2O_4$ solid solutions can be obtained [3]. To describe correctly the processes occurring at the interface during crystallization of thin film heterostructures the thermodynamic properties of $MgGa_2O_4$ in a wide temperature range are required.

Inverse spinels are known to demonstrate complex disordering phenomena involving important consequences both for their thermochemical and physical properties. According to Schwarz et al. [4] the thermal diffusivity of single crystal $MgGa_2O_4$ was rising significantly at temperatures above 950 °C. Galazka et al. [1] observed a transition from the inverse spinel structure to the random one, which is accompanied by an endothermic bend on a DSC curve at the temperature near 1000 °C.

Wilkerson et al. [5] studied heat capacity of magnesium gallate by DSC in temperature range 298.15–673 K and the standard deviation in the measurement was on average 6.0%. Navrotsky and Kleppa [6] determined enthalpy of formation from the oxides $\Delta_{ox}H^0(MgGa_2O_4, 970\,K) = -40.2 \pm 1.2\,kJ\,mol^{-1}$ by solution calorimetry in molten oxides solvent ($9PbO{\cdot}3CdO{\cdot}4B_2O_3$) at 970 K. Low temperature heat capacity data for $MgGa_2O_4$ were not found in the literature.

The aim of the present study was the experimental study of the heat capacity of $MgGa_2O_4$ and calculation of thermodynamic functions (heat capacity, enthalpy change, entropy) in the temperature range 0–1200 K.

2. Experimental

2.1. Synthesis

Magnesium gallate specimen was prepared by self-propagating high temperature synthesis as described in [3]. The initial water solution containing citric acid monohydrate

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Table 1
Characterization of chemical samples used in this study and synthesized sample.

Chemical name	Chemical formula	Source	Mass fraction purity	Analysis method
Magnesium nitrate hexahydrate	$Mg(NO_3)_2{\cdot}6H_2O$	Reachim (Russia)	≥0.99	–
Gallium(III) nitrate octahydrate	$Ga(NO_3)_3{\cdot}8H_2O$	CJSC "Novosibirsk rare metals plant" (Russia)	≥0.995	–
Citric acid monohydrate	$(HOOCCH_2)_2C(OH)COOH{\cdot}H_2O$	Reachim (Russia)	≥0.995	–
Magnesium gallate	$MgGa_2O_4$	Synthesis	≥0.99 single-phase	ICP-MS XRD

$(HOOCCH_2)_2C(OH)COOH{\cdot}H_2O$ and a stoichiometric mixture of $Mg(NO_3)_2{\cdot}6H_2O$ and $Ga(NO_3)_3{\cdot}8H_2O$ (all reagents were of analytical grade and applied as received without further purification) was evaporated under continuous stirring to form a gel. Further heating of reaction mass was accompanied by a self-propagating combustion reaction spreading over the entire volume (in 1–2 min) with the formation of a white finely dispersed powder. The thermal treatment of obtained precursor at 1173 K resulted in the formation of $MgGa_2O_4$ with cubic spinel structure.

The characterization of the sample was performed by X-ray diffraction and inductively coupled plasma-mass spectrometry (ICP-MS).

X-ray diffraction analysis (Bruker D 8 Advance diffractometer, $CuK\alpha_1$-radiation, λ = 1.5406 Å, LYNXEYE detector, reflection geometry) demonstrated that only reflections attributable to the synthesized $MgGa_2O_4$ were observed (Supplement, Fig. S1). The calculated unit cell parameter of $MgGa_2O_4$ (a = 8.287 Å) was in a good agreement with literature data [7]. The average crystallite size was estimated to be about 40 nm.

Inductively coupled plasma-mass spectrometry was performed on an Agilent 7500ce spectrometer (Agilent Technologies, USA). Based on the experimental data it was found that the ratio of elements Mg: Ga is equal to 0.998:1.002. The final purity of the $MgGa_2O_4$ sample was established to be >99.0% (see Table 1).

2.2. Heat capacity measurements

2.2.1. Adiabatic calorimetry

The temperature dependence of the heat capacity of $MgGa_2O_4$ was measured using adiabatic vacuum calorimeter BKT-3 ("Termis", Russia) in the temperature range from 6.93 K to 347.06 K. All measurements were carried out in an automatic mode using an automatic computer-interfaced calorimeter with an analog control/data acquisition system. The calorimetric ampoule is a thin-walled titanium cylindrical container (1 cm^3 in inner volume and approximately 1.60×10^{-3} kg in mass) with a screwed bronze cap and an indium sealing gasket. The temperature was measured with an iron-rhodium resistance thermometer (resistance $R \approx 100$ ohm) calibrated in the Russian Research Institute of Physical and Radio Technical Measurements of Russian State Agency of Standards using the ITS-90 scale. The sensitivity of a thermometric circuit was 10^{-3} K, and the standard uncertainty for the temperature measurements was $u(T)$ = 0.01 K. The design of the calorimetric setup and the measurement procedure has been described in detail by Malyshev et al. [8]. To validate the measurement procedure, the heat capacities of special-purity copper (OSCH 11-4, copper content >99.999 wt.%), standard synthetic corundum (purity >99.999 wt.%) and K-2 benzoic acid (purity >99.99 wt.%) purchased from metrological institutions of the State Standard Committee of the Russian Federation were measured in the range from 5 to 350 K. The relative standard uncertainties for the heat capacity measurements for the reference substances were $u_r(C_p)$ = 0.02 at T < 15 K, $u_r(C_p)$ = 0.005 in the temperature range from 15 to 40 K, and $u_r(C_p)$ = 0.002 between 40 and 350 K.

The mass of the specimen was 1.00773 ± 0.00005 g. Molecular weight of $MgGa_2O_4$ calculated using the atomic mass values from [9] is 227.7486 g mol^{-1}. Experimental heat capacity data obtained by adiabatic calorimetry in the range 6.93–347.06 K are presented in Table S1.

2.2.2. Differential scanning calorimetry

The measurements of $MgGa_2O_4$ heat capacity at high temperatures were carried out in platinum crucibles equipped with lids in a flow (10 mL min^{-1}) of dry argon (purity, 99.9995 wt.%) at a heating rate of 20 K min^{-1}, using a differential scanning calorimeter NETZSCH 449 F1 Jupiter®. Prior to the sample heat capacity measurements a few cycles of pumping out and filling with inert gas of the entire volume of a furnace and a balance were carried out. The synthetic sapphire (supplied by NETZSCH-Gerätebau; purity, 99.99%) was used as the reference substance. The standard uncertainty for the temperature was $u(T)$ = 0.5 K.

The calibration of the calorimeter demonstrated that the heat capacity measurement uncertainty corresponded to the instrument specifications and was not exceed 2.85% throughout the study temperature range.

The weight of the sample was 35.01 mg. The relative standard uncertainty for the experimental heat capacity values was $u_r(C_p)$ = 0.03 in the temperature range 321.9–1201.9 K.

A comparison of data obtained by adiabatic and differential scanning calorimetry revealed that the values of high-temperature heat capacity were systematically higher than the low-temperature data. Therefore, to joint the low- and high-temperature heat capacity data between 300 and 400 K, the values of $C_p(T)$ obtained by DSC were reduced by 2.5 J K^{-1} mol^{-1}. The revised experimental values of the heat capacity of $MgGa_2O_4$ in the temperature range 321.9–1201.9 K are presented in Table S2.

3. Experimental data treatment

The temperature dependence of heat capacity of $MgGa_2O_4$ in the 6.93–347.06 K range was a monotonic increasing curve with any peculiarities (Fig. 1). Revealed at very low temperatures weak waves on the $C_p(T)$ (inset in Fig. 1) are not related to heat capacity anomaly. We assume that it was caused by the dramatic decrease of the ratio $C_p^{sample}/[C_p^{sample} + C_p^{ampoule}]$. According to the experimental data, the ratio $C_p^{sample}/[C_p^{sample} + C_p^{ampoule}]$ varied from 0.08 to 0.1 in the temperature range 7–20 K. Consequently, the experimental uncertainty for the low-temperature $C_p(T)$ data tended to be significantly larger than those obtained for reference substances (synthetic corundum and K-2 benzoic acid). Therefore, in this case the relative standard uncertainty was assumed to be ±13% between 7 and 20 K. In the same time, the high experimental uncertainty decreased with increasing temperature and vanished above 20 K. Its value has been found to be equal to ±1% between 20 and 50 K and ±0.5% in the range 50–347 K. Nevertheless, we gave these experimental points in order to demonstrate, that no sufficient heat capacity anomalies proceeds in the range below 20 K.