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A systematic study on crystal structure and magnetic properties of Ln_3GaO_6 ($Ln = Nd$, Sm, Eu, Gd, Tb, Dy, Ho and Er)

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Abstract

The crystal structures of a series of compounds with the composition $Ln_3GaO_6(Ln=Nd, Sm, Eu, Gd, Tb, Dy, Ho$ and Er) synthesized by solid-state reaction at 1400°C are investigated. X-ray diffraction shows that Ln_3GaO_6 has a non-centrosymmetric orthorhombic structure (space group $Cmc2_1$). Lattice parameters a, b, c and cell volume and the average distances between $Ln(1)-O$, $Ln(2)-O$ of these compounds decrease with the decreasing of the radii of trivalent Ln ions, which accord with the expected lanthanide contraction behavior. There are two sites of seven-fold coordination for Ln atoms with oxygens, and Ga atoms are in oxygen tetrahedra which are distorted and elongated along the *a*-axis. Magnetization measurements indicate that the susceptibility χ changes with temperature in Curie-type manner.

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1. Introduction

There exist four definite compounds, $Ln_3Ga_5O_{12}$, $LnGaO₃$, $Ln₄Ga₂O₉$ and $Ln₃GaO₆$ in the rare earth (Ln) oxides and gallium oxide pseudo-binary systems [\[1–3\]](#page-5-0), Single crystals of $Ln_3Ga_5O_{12}$, which is well known as gallium garnet with the space group cubic $Ia\bar{3}d$ [\[4\]](#page-5-0), are used as substrate material for yttrium iron garnets (YIG) film reported by several authors [\[5–7\]](#page-6-0). $Ln_3Ga_5O_{12}$ was found in most of the Ln –Ga oxides pseudo-binary system, while $LnGaO₃$ compounds were reported only in $Ln = La$, Ce, Pr, Nd, with distorted perovskite structure. Nicolas et al. [\[3\]](#page-5-0) reported that short melting and overheating of the melt using the laser device yield pure $SmGaO₃$ and $GdGaO₃$ isostructural with $GdFeO₃$ (*Pbnm*). The monoclinic phase of $Ln_4Ga_2O_9$ ($Ln = La$, Nd, Sm, Eu and Gd) are isostructural with $Eu₄Al₂O₉ [8]$ $Eu₄Al₂O₉ [8]$.

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The $Gd_4Ga_2O_9$ is stable only at high temperature $(T>1490^{\circ}C)$ and melts incongruently, whereas $Sm_4Ga_2O_9$ is synthesized above 1200°C [\[3\]](#page-5-0). The orthorhombic compounds Ln_3GaO_6 were prepared with $Ln=Nd$, Sm, Gd, Tb, Dy, Ho and Er. According to the phase diagrams of Sm_2O_3 – Ga_2O_3 and Gd_2O_3 – Ga_2O_3 [\[3\]](#page-5-0), Sm_3GaO_6 and Gd_3GaO_6 have non-congruent melting points at 1715° C and 1760° C, respectively, and melt to $Ln₂O₃$ and liquid. Many authors have reported the lattice parameters: $a = 11.400 \text{ Å}, b = 5.515 \text{ Å}$ and $c = 9.07 \text{ Å}$ for Sm_3GaO_6 , $a = 11.278 \text{ Å}$, $b = 5.480 \text{ Å}$ and $c = 8.99 \text{ Å}$ for Gd_3GaO_6 [\[3\]](#page-5-0), and $a = 11.53 \text{ Å}$, $b = 5.57 \text{ Å}$ and $c = 9.17 \text{ Å}$ for Nd₃GaO₆ [\[9\],](#page-6-0) but only the crystal structure of Gd_3GaO_6 was solved by Yamane et al. ($a = 8.993 \text{ Å}, b = 11.281 \text{ Å}$ and $c = 5.481 \text{ Å}$) [\[10\]](#page-6-0). In the present study, we synthesized a serials of Ln_3GaO_6 $(Ln=Nd, Sm, Eu, Gd, Tb, Dy, Ho and Er) compounds,$ which are isostructural with $Gd_3GaO_6(Cmc2_1)$, and refined their crystal structure using X-ray powder diffraction data by means of Rietveld refinement technique, magnetization and electrical resistance measurements are also carried out in some of the compounds.

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Polycrystalline $Ln_3GaO_6(Ln=Nd, Sm, Eu, Gd, Tb,$ Dy, Ho and Er) samples were prepared by a solid-state reaction. The starting materials are high purity $(>99.9\%)$ Nd₂O₃, Sm₂O₃, Eu₂O₃, Gd₂O₃, Tb₂O₃, Dy_2O_3 , Ho_2O_3 , Er_2O_3 and Ga_2O_3 . The raw powder was preheated separately at 200° C for 5h and weighed according to the stoichiometric compositions, calcined at 900° C for 12h in air, and then ground and pressed into pellets. The pellets were sintered in a siliconmolybdenum stove at 1400° C for 4 h in air, then down to 1200° C for 24 h. Finally, the samples were quenched to room temperature in the air.

Fig. 1. X-ray diffraction patterns of Ln_3GaO_6 ($Ln = Nd$, Sm, Eu, Gd, Tb, Dy, Ho, Er).

X-ray powder diffraction (XRD) data used for structural analysis were collected on a Rigaku D/max 2500 diffractometer with CuK α radiation (50 kV \times 250 mA) and a graphite monochromator. A step scan mode was employed with a step width of $2\theta = 0.02^{\circ}$ and a sampling time of 1 s. The XRD patterns showed that the compounds are single phase with minor impurity phase. The XRD data were analyzed by the Rietveld refinement program FullProf.2k (Version 2.40) [\[11\]](#page-6-0) based on the structure model of Gd_3GaO_6 reported by Yamane et al. [\[10\],](#page-6-0) Pseudo-Viogt function is used as the profile function.

The temperature dependence of magnetization in a field of 1 kOe in the range of 5–300 K was measured by a superconducting quantum interference device (SQUID) magnetometer.

3. Results and discussion

3.1. Structure refinement

The XRD data of the compounds Ln_3GaO_6 ($Ln = Nd$, Sm, Eu, Gd, Tb, Dy, Ho and Er) in the 2θ region between 10° and 120° were used for the refinement (Fig. 1). There are minor impurity phase (about 1–4%) which could be identified as $\text{Ln}_3\text{Ga}_5\text{O}_{12}$ or $\text{Ln}_4\text{Ga}_2\text{O}_9$. The X-ray data of main phase could be completely indexed on the basis of orthorhombic space group $Cmc2₁$. Table 1 shows the final results of R factors of the Rietveld refinements and lattice parameters of the compounds $Ln_3GaO_6(Ln=Nd, Sm, Eu, Gd, Tb, Dy,$ Ho and Er). Typical best fit of X-ray profile are shown in [Fig. 2.](#page-2-0) The vertical bars at the middle indicate the expected Bragg reflection positions, and the lowest curve is the difference between observed and calculated patterns.

[Fig. 3](#page-2-0) shows the lattice parameters a, b, c of the compounds Ln_3GaO_6 vs. radii of trivalent Ln ions. The

Table 1 Final results of the Rietveld refinements for the Ln_3GaO_6 ($Ln = Nd$, Sm, Eu, Gd, Tb, Dy, Ho, Er) compounds in space group $Cmc2_1$

Ln	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er
Radius for Ln^{3+} (Å)	1.109	1.079	1.066	1.053	1.04	1.027	1.015	1.004
$R_{\rm wp}$ (%)	9.65	10.2	11.8	10.3	10.3	10.6	11.1	10.5
$R_{\rm p}$ (%)	7.76	8.07	9.65	8.40	8.73	8.60	9.12	7.91
$R_{\rm exp}$ (%)	5.55	6.02	6.96	6.36	5.59	5.93	3.99	3.40
$R_{\rm B}$ (%)	4.02	3.31	4.80	4.00	4.16	3.58	4.88	5.13
$R_{\rm F}$ (%)	2.75	2.88	4.34	3.91	3.47	3.21	4.00	3.94
S	1.74	1.70	1.70	1.62	1.84	1.79	2.78	3.09
a(A)	9.1820(1)	9.0743(1)	9.0284(1)	8.9911(1)	8.9344(1)	8.8875(1)	8.8451(1)	8.8009(1)
$b\left(\check{A}\right)$	11.5396(1)	11.4070(1)	11.3420(1)	11.2801(1)	11.2153(1)	11.1512(1)	11.0931(1)	11.0345(1)
c(A)	5.5748(1)	5.5181(1)	5.4954(1)	5.4796(1)	5.4447(1)	5.4217(1)	5.4027(1)	5.3802(1)
$V(A^3)$	590.690(4)	571.183(3)	562.731(3)	555.746(4)	545.567(3)	537.332(2)	530.116(3)	522.495(4)
Density, calculated (g/cm^3)	6.729	7.172	7.337	7.618	7.822	8.074	8.275	8.485

Fig. 2. Observed, calculated and difference XRD patterns of Tb_3GaO_6 . The middle vertical bars indicate Bragg reflection positions.

Fig. 3. Lattice parameters of $Ln_3GaO_6(Ln=Nd, Sm, Eu, Gd, Tb, Dy,$ Ho, Er) vs. radii of trivalent Ln ions.

lattice parameters a, b and c decrease with the decreasing of the radii of trivalent Ln ions. The unitcell volume (Fig. 4) clearly shows the expected lanthanide contraction behavior, i.e., it exhibits a linear relationship when plotted vs. the ionic radii of trivalent rare-earth ions. The lattice parameters of $Nd₃GaO₆$, $Sm₃GaO₆$ and $Gd₃GaO₆$ determined in present work agree well with the former reported data [\[3,9,10\].](#page-5-0) The structure of Ln_3GaO_6 is shown in Fig. 5. There are four formula units per unit cell, i.e., the unit cell contains $12Ln + 4Ga + 24O$. The ions Ln, Ga and oxygens occupy $8(b) + 4(a)$, $4(a)$ and two $8(b) +$ two $4(a)$, respectively. The equivalent sites and atomic coordinates of these compounds are listed in [Table 2.](#page-3-0) Because all of the z coordinates of atoms are variable, so we fix the z coordinate of Ga to zero.

The selected interatomic distances and coordination numbers of the orthorhombic Ln_3GaO_6 compounds are listed in [Table 3](#page-4-0). There are two sites of seven-fold

Fig. 4. Unit-cell volume and average distances of Ln–O of $Ln_3GaO_6(Ln=Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er)$ vs. radius of trivalent *Ln* ions.

Fig. 5. The structure of Ln_3GaO_6 showing GaO_4 tetrahedra.

coordination for Ln atoms with oxygens (Wyckoff position $8b$ for Ln1 and $4a$ for Ln2). For the different rare-earth ions investigated the average interatomic distances between the $Ln(1)$ and O atoms are in the range 2.34–2.47 \AA and the average interatomic distances between the $Ln(2)$ and O atom are in the range 2.33–2.44 Å. The average distances between $Ln(1)-O$, $Ln(2)$ –O, which are particularly sensitive to the lanthanide contraction, decrease with the decreasing of the radii of trivalent Ln ions (see Fig. 4). Ga atoms are in oxygen tetrahedra which are distorted and elongated along the a -axis. The average lengths of the Ga–O bonds are in the range $1.82-1.86$ Å. Selected bond angles of the O–Ga–O in the tetrahedron are also shown in [Table 4](#page-4-0),

Data derived from Yamane et al. [\[10\].](#page-6-0)

which are closely equal to the result of Gd_3GaO_6 of Yamane et al. [\[10\]](#page-6-0). Oxygen atoms on O(2) site coordinate only to Ln atoms, and the shortest $Ln-O$ distances for the combination of Ln and O(2) atoms $(Ln(1)-O(2))$ 2.10–2.21 Å and $Ln(2)$ –O(2) 2.24 \sim 2.37 Å), which are also sensitive to the lanthanide contraction and shrink with the decreasing of the radii of trivalent Ln ions.

To examine the reliability of the determined structure, we used the bond valence model to estimate the bond valence of the ions ([Table 5\)](#page-5-0) by Brown's empirical relationship between bond valence and interatomic distance [\[12\].](#page-6-0) The bond valences of all the ions are close to their chemical valence. The crystal structure of $Ln₃GaO₆$ obtained in this work is isostructural with Gd_3GaO_6 [\[10\],](#page-6-0) but they are disparity in atomic parameters. The atoms must adjust to their atomic parameters to adapt to the change of radii and electron

affinity of Ln ions. In the base of bond valences of all ions, our results seem more reasonable (see [Table 5](#page-5-0)). So we conclude that the structure refined by our Rietveld refinement is reliable.

3.2. Magnetization

Magnetization measurements were also performed from 5K to room temperature for $Nd₃GaO₆$ and Tb₃GaO₆. The measured magnetic susceptibility χ is shown in [Fig. 6,](#page-5-0) which indicates that χ changes with temperature in a Curie-type manner. The data can be fitted to a Curie–Weiss law of general formula:

$$
\chi = \chi_0 + C_g/(T + \Theta),
$$

where χ_{0} and Θ are the temperature-independent susceptibility and Weiss constant, and C_g the Curie

Atoms	Coordination number	Ln(A)							
		Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er
$Ga-O(3)$	$1\times$	1.76(2)	1.77(2)	1.78(2)	1.78(2)	1.75(2)	1.78(2)	1.71(2)	1.77(2)
$Ga-O(4)$	$1\times$	1.79(2)	1.80(2)	1.79(2)	1.82(2)	1.80(2)	1.80(2)	1.84(2)	1.81(2)
$Ga-O(1)$	$2\times$	1.93(2)	1.86(2)	1.92(2)	1.85(2)	1.89(2)	1.90(2)	1.89(2)	1.92(2)
Average		1.85	1.82	1.85	1.82	1.83	1.84	1.83	1.86
$Ln(2)-O(2)$	$2\times$	2.37(2)	2.35(2)	2.32(2)	2.32(2)	2.31(2)	2.27(2)	2.28(2)	2.24(2)
$Ln(2)-O(2)$	$2\times$	2.41(2)	2.36(2)	2.38(2)	2.32(2)	2.32(2)	2.32(2)	2.30(2)	2.28(2)
Ln(2)O(1)	$2\times$	2.51(2)	2.48(2)	2.48(2)	2.46(2)	2.44(2)	2.44(2)	2.41(2)	2.34(2)
$Ln(2)-O(4)$	$1\times$	2.53(2)	2.52(2)	2.49(2)	2.50(2)	2.45(2)	2.47(2)	2.48(2)	2.57(2)
Average		2.44	2.41	2.40	2.39	2.37	2.37	2.35	2.33
$Ln(1)-O(2)$	$1\times$	2.21(2)	2.20(2)	2.19(2)	2.18(2)	2.18(2)	2.17(2)	2.17(2)	2.10(2)
$Ln(1)-O(2)$	$1\times$	2.34(2)	2.33(2)	2.30(2)	2.32(2)	2.28(2)	2.28(2)	2.25(2)	2.25(2)
$Ln(1)-O(1)$	$1\times$	2.37(2)	2.34(2)	2.36(2)	2.33(2)	2.31(2)	2.29(2)	2.29(2)	2.30(2)
$Ln(1)-O(1)$	$1\times$	2.46(2)	2.43(2)	2.36(2)	2.40(2)	2.37(2)	2.35(2)	2.35(2)	2.32(2)
$Ln(1)-O(4)$	$1\times$	2.50(2)	2.44(2)	2.43(2)	2.41(2)	2.40(2)	2.38(2)	2.39(2)	2.36(2)
$Ln(1)-O(3)$	$1\times$	2.69(2)	2.65(2)	2.61(2)	2.59(2)	2.60(2)	2.54(2)	2.52(2)	2.50(2)
$Ln(1)-O(3)$	$1\times$	2.69(2)	2.65(2)	2.64(2)	2.64(2)	2.61(2)	2.62(2)	2.57(2)	2.58(2)
Average		2.47	2.44	2.41	2.41	2.39	2.38	2.36	2.34

Table 4 Bond angles of O–Ga–O in Ga–O coordination tetrahedron for the Ln_3GaO_6 ($Ln = Nd$, Sm, Eu, Gd, Tb, Dy, Ho, Er) compounds

constant given by the relation

$$
C_{\rm g}=N\mu_{\rm eff}^2/3\,k,
$$

where N is the number of ions that carry a magnetic moment per unit cell, μ_{eff} the effective moment of the magnetic ion, and k the Boltzman constant. The parameters χ_{0} , C_{g} , and Θ were determined by a leastsquares fit for the temperature range 60–300 K. The values of the magnetic moments and the Weiss constant deduced from the fits are reported in [Table 6.](#page-5-0) The plot of $(\chi - \chi_0)^{-1}$ vs. T [\(Fig. 6](#page-5-0)) produces a straight lines as expected for a Curie-type behavior except for $Ln = Nd$ compound which showed a slightly deviation from the Curie law below 60 K as shown in [Fig. 6b.](#page-5-0) This anomaly at low temperature may arise from a small amount of antiferromagnetic impurity phase. Electrical resistance was measured by the standard four-probe method, the resistivities of Ln_3GaO_6 samples are larger than

Table 5 Bond valence of the Ln_3GaO_6 ($Ln = Nd$, Sm, Eu, Gd, Tb, Dy, Ho, Er)

Ln	Ln(1)	Ln(2)	Ga	O(1)	O(2)	O(3)	O(4)		
Nd	2.916	2.884	2.961	1.826	2.177	1.761	1.870		
Sm	2.993	2.973	3.161	1.950	2.239	1.790	1.954		
Eu	3.039	2.924	2.952	1.870	2.237	1.787	1.952		
Gd	3.029	3.005	3.110	1.953	2.258	1.795	1.956		
Gd^a	3.421	2.955	2.887	2.129	2.385	1.799	1.859		
Tb	2.845	2.864	3.096	1.862	2.116	1.802	1.893		
Dy	2.738	2.674	2.982	1.774	2.004	1.704	1.872		
Ho	2.998	2.949	3.095	1.908	2.201	1.723	2.098		
Er	2.892	2.919	2.894	1.861	2.037	1.716	2.085		

^aCalculated from Yamane et al. [\[10\]](#page-6-0).

Fig. 6. The magnetic susceptibility in a field of 1 kOe as a function of temperature for Ln_3GaO_6 : (a) $Ln = Tb$ and (b) $Ln = Nd$.

Table 6 List of the parameters obtained from a fit to a Curie–Weiss law

Ln C_{φ}	Θ	χ_0 $(K$ emu/mol) (K) $(10^{-3}$ emu/mol) (obs) (cal) interval (K)		$\mu_{\rm eff}$ $\mu_{\rm eff}$ Fitting
Tb 33.62 Nd 3.65	11.60 2.74 14.28 2.03			9.47 9.72 $60-300$ 3.12 3.62 $60-300$

200 M Ω cm. It shows that Ln_3GaO_6 serial compounds are insulators.

4. Conclusion

Detailed structural data for carefully prepared Ln_3GaO_6 ($Ln = Nd$, Sm, Eu, Gd, Tb, Dy, Ho and Er, space group $Cmc2_1$) compounds are reported in this work. The Rietveld refinement of the X-ray diffraction data show that lattice parameter a, b, c and cell volume of these compounds and the average distances between $Ln(1)-O$, $Ln(2)-O$ decrease with the decreasing of the radii of trivalent Ln ions, which accord with the expected lanthanide contraction behavior. There are two sites of seven-fold coordination for Ln atoms with oxygens, and Ga atoms are in oxygen tetrahedra which are distorted and elongated along the a-axis. Magnetization for this series of compounds clearly reflects paramagnetism. The magnetic susceptibility χ changes with temperature in a Curie-type manner.

Acknowledgments

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