Crystal structure of galotrilanthanum triiodide, La_3GaI_3

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Abstract

GaI_3La_3 , cubic, $I4_132$ (No. 214), $a = 12.666(2) \text{ \AA}$, $V = 2032.0 \text{ \AA}^3$, $Z = 8$, $R_{\text{gt}}(F) = 0.068$, $wR_{\text{ref}}(F^2) = 0.131$, $T = 293 \text{ K}$.

Source of material

The title compound was synthesized from stoichiometric mixtures of La, LaI_3 and Ga under Ar atmosphere in sealed Ta ampoule at 1173 K for 20 days. As the reactants and the product are air and moisture sensitive, all handling was carried out under Ar atmosphere inside a glove box or through the Schlenk technique.

Discussion

Reduced rare-earth halides have been of continuous interest because of their unusual physical properties such as superconductivity and magnetic ordering [1–3]. Recently we have reported the synthesis and structural determination of a series of these compounds which have the stoichiometry $\text{La}_3\text{X}_3\text{Z}$ where $\text{X} = \text{Br}, \text{I}$ and $\text{Z} = \text{Si}, \text{P}, \text{As}, \text{Sb}, \text{C}_2$ [4]. Many of these solids crystallize in the cubic space group $I4_132$ and are isostructural to $\text{Gd}_3\text{Cl}_3\text{C}$ [5]. The building unit of this type of structure is the main group element Z centering octahedron of La. Single crystal structures of this type of compounds with group 13 elements as the interstitial Z, however, have not been described previously in the literature. In this contribution we present the single crystal structure of La_3GaI_3 . As described elsewhere [4,5], the structure consists of edge-sharing La_6 octahedra helically propagating in three dimensions. Ga is at the center of these octahedra. The figure shows such a helix along the a -direction. For clarity, the iodine atoms are omitted. They cap the corners and edges of the octahedra. The traveling of the helices in other directions is similar. The La_6 octahedron is distorted with the shared edge being shorter ($d(\text{La}—\text{La}) = 4.059(5) \text{ \AA}$) compared to the unshared edges ($d(\text{La}—\text{La}) = 4.279(2) \text{ \AA}, 4.377(1) \text{ \AA}$). One of the reasons for the distortion is the repulsion between the highly charged Ga atoms in adjacent octahedra. The apparent charge of Ga derives from the formal electronic partitioning of $(\text{La}^{3+})_3\text{Ga}^{5-}(\Gamma)_3 \cdot e^-$. As a result of the repulsion, the Ga—Ga distance between the adjacent octahedra is $4.4779(8) \text{ \AA}$, compared to the sum of the atomic radii of Ga ($1.25 \text{ \AA} + 1.25 \text{ \AA} = 2.50 \text{ \AA}$). The Ga to La distance is $3.022(2) \text{ \AA}$, close to the sum of the covalent radii of Ga ($1.25 \text{ \AA}$) and La ($1.69 \text{ \AA}$), and indicates strong covalency.

Table 1. Data collection and handling.

Crystal:	metallic dark grey fragment, size $0.02 \times 0.04 \times 0.04 \text{ mm}$
Wavelength:	$\text{Mo K}\alpha$ radiation ($0.71073 \text{ \AA}$)
μ :	240.15 cm^{-1}
Diffraction, scan mode:	Siemens SMART CCD, ω
$2\theta_{\text{max}}$:	46.5°
$N(hkl)_{\text{measured}}, N(hkl)_{\text{unique}}$:	4123, 237
Criterion for $I_{\text{obs}}, N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 237
$N(\text{param})_{\text{refined}}$:	15
Programs:	SADABS [6], SHELXTL [7]

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Table 2. Atomic coordinates and displacement parameters (in Å²).

Atom	Site	x	y	z	U ₁₁	U ₂₂	U ₃₃	U ₁₂	U ₁₃	U ₂₃
La	24h	1/8	0.6133(1)	−y+1/4	0.034(1)	0.044(1)	U ₂₂	−0.0079(6)	U ₁₂	−0.005(1)
I	24g	1/8	0.8853(1)	−y+1/4	0.035(2)	0.043(1)	U ₂₂	−0.0015(7)	−U ₁₂	−0.008(2)
Ga	8b	7/8	7/8	7/8	0.034(2)	U ₁₁	U ₁₁	−0.005(2)	U ₁₂	U ₁₂

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