Table 3. Optical properties

<table>
<thead>
<tr>
<th></th>
<th>Ho$_3$Ga$_2$(GaO$_4$)$_3$</th>
<th>Yb$_3$Al$_2$(AlO$_4$)$_3$</th>
<th>Dy$_3$Al$_2$(AlO$_4$)$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$a_0$(Å)</td>
<td>12.2813 ± 0.0003</td>
<td>11.9295 ± 0.0002</td>
<td>12.0381 ± 0.0003</td>
</tr>
<tr>
<td>$V$(Å$^3$)</td>
<td>1852.4 ± 0.1</td>
<td>1697.8 ± 0.1</td>
<td>1744.3 ± 0.2</td>
</tr>
<tr>
<td>$D_z$(g/cm$^3$)</td>
<td>7.432</td>
<td>7.781</td>
<td>8.020</td>
</tr>
<tr>
<td>$Z$</td>
<td>8</td>
<td>8</td>
<td>8</td>
</tr>
</tbody>
</table>

was provided by S. Mroczkowski. Dy$_2$O$_3$, 99-999% and Al$_2$O$_3$, 99-999% reagents were used.

Chemical characterization

Wanklyn reports rare-earth impurities in the range of 0-01 to 1% as characterized by spectrographic and electron spin resonance (e.s.r.) analysis. Mroczkowski stated that less than 0.01% Dy$^{3+}$ substituted for Al$^{3+}$ and used e.s.r. for characterization.

Crystal geometry

All the rare-earth garnets studied are body-centered cubic, space group $Ia3d$. The cell constants and standard error (Table 1) were obtained from X-ray diffraction powder data with a least-squares indexing and refinement program (Evans, Appleman & Handwerker, 1963) which employs unweighted $\Delta\theta$ residuals.

Powder data were obtained as relative peak heights read from strip-chart recordings prepared at 24°C with Ni filtered Cu K$_\alpha$ radiation and a diffractometer scanned at $\frac{1}{2}$ ° (2θ)/min. The specimens were smear mounted and contained α-quartz as an internal standard, angular data for which were taken from Frondel (1962). The $d$ values listed in Table 1 are weighted averages of the values obtained separately from Cu K$_{\alpha_1}$ (1.54051 Å) and Cu K$_{\alpha_2}$ (1.54433 Å) when the two peaks were resolved. When they were not, a single $d$ value was calculated with the weighted average of the Cu K$_\alpha$ wavelengths, 1.54178 Å.

Absolute intensities were characterized by comparison of largest peak intensities with those of Al$_2$O$_3$ (Linde Type A) in an equal-weight mixture with the material being characterized (de Wolff, 1961, Private communication; see

* Present address: IBM Research Laboratory, San Jose, California 95114, U.S.A.

References


X-ray data for (+)$_D$-sodium bis(oxalato)ethylendiaminecobaltate(III) tetrahydrate. By G. WILLIAM SVETICH and DENNIS S. DELORME, University of North Dakota, Chemistry Department, Grand Forks, North Dakota 58201, U.S.A.

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Origin of specimens

The procedure of Dwyer, Reid & Garvin (1961) was modified for the preparation of (+)$_D$-Na[Co(ox)$_2$en]$.4$$H_2$$O$, where ox = C$_2$O$_4^{2-}$ and en = NH$_2$CH$_2$CH$_2$NH$_2$, by Stadtherr (1970). The resolution was carried out by the method of Dwyer et al. (1961) using (-)$_D$-Na[Co(en)$_2$ox]Cl.$H_2$O. The specific rotation was identical to that reported by Dwyer et al. Crystals were obtained by recrystallization from water.

Crystal geometry

$h/1$ through $h/4l$ Weissenberg photographs and both zero and first level precession photographs about $a^*$ and $c^*$ axes
were obtained with nickel-filtered copper radiation \([\lambda(K\alpha)=1.54178\ \text{Å}]\). Systematic absences observed are:

\[
\begin{array}{ll}
hkl & h + l \neq 2n \\
0kl & l \neq 2n \\
h\bar{0}l & h + l \neq 2n \\
hk0 & h \neq 2n \\
h00 & h \neq 2n \\
o0l & l \neq 2n \\
o01 & l \neq 2n \\
\end{array}
\]

The crystals are orthorhombic with space group \(B22_12\).

The cell data are:

\[
\begin{align*}
& a = 11.942 \pm 0.007 \ \text{Å} \\
& b = 16.874 \pm 0.031 \\
& c = 7.535 \pm 0.009 \\
& Z = 4, \ M.W. = 390-1238 \\
& D_m = 1.699 \ \text{g.cm}^{-3} \\
& D_x = 1.706 \ \text{g.cm}^{-3} \\
\end{align*}
\]

No further work is planned on this compound.

References


(Received 14 October 1970; accepted 7 December 1970)

Origin of specimens

The single crystals used in this study were grown and characterized by Dr B. Brezina of the Institute of Physics, Czechoslovak Academy of Sciences, Prague. A description of the crystal growth and morphology may be found in Brezina, Smutny, Janovsek & Moreck (1969).

Crystal chemistry

Shirane, Jona & Pepinsky (1955) indicated that the space group of lithium thallium tartrate monohydrate, \(\text{LiTI} (\text{C}_4\text{H}_4\text{O}_6).\text{H}_2\text{O} \) (LTT) was \(P2_12_12\) by analogy to the isomorphous lithium ammonium tartrate monohydrate (LAT). A detailed crystal structure analysis has not yet been performed. Rough cell parameters were recently determined by Brezina \textit{et al.} (1969). These values were used as trial parameters for a refinement based on twenty-seven unambiguously indexed reflections. The cell parameters and their standard deviations were obtained from a least-square refinement of the variance-covariance matrix derived from the unweighted \(\Delta\theta\) residuals (Evans, Appleman & Handwerker, 1963). The results are compared in Table 1.

Powder data

Single crystals of LTT were ground under acetone and mounted with collodion to prevent alteration of water of crystallization content. Powder data were taken on a diffractometer at 20°C using Ni-filtered Cu K\(\alpha\) radiation (Table 1). The diffractometer was calibrated with a high purity silicon standard \((a_0 = 5.4301 \ \text{Å})\). Peak heights were used to derive relative intensity values.

Crystal physics

LTT shows a remarkable dielectric anomaly at 10°K. Ferroelectricity was first reported by Matthiessen & Hulm (1951). It possesses a spontaneous polarization of 0.14 microcoulomb cm\(^{-2}\) along the \(a\) axis at 1.3°K. However, in contrast to ordinary ferroelectrics which show a pronounced peak in the dielectric constant at the Curie temperature, the low-frequency dielectric constant of LTT is almost constant (about 5 \(\times\) 10\(^3\)) at and below the Curie temperature. Recent studies by Fousek, Cross & Seeley (1970) and Sawaguchi & Cross (1971) have shown that the dielectric constant and the elastic constant are strong functions of applied d.c. bias and that an electromechanical coupling effect is extraordinarily high. The piezoelectric constant near the Curie temperature \((d_{14} \approx 10^8 \ \text{coulomb \ newton}^{-1})\) seems to be the highest of any known ferroelectric material. The crystal data on the low temperature ferroelectric phase have not been measured.

Comparison with related structures

Lithium thallium tartrate monohydrate in its room temperature form is isostructural with lithium ammonium tartrate monohydrate, \(\text{LiNH}_2(\text{C}_4\text{H}_4\text{O}_6).\text{H}_2\text{O} \) (LTT) and lithium rubidium tartrate monohydrate, \(\text{LiRb}(\text{C}_4\text{H}_4\text{O}_6).\text{H}_2\text{O} \) (Shirane \textit{et al.}, 1955). All these compounds share the same group \((P2_12_12\) and similar \(b_0\) and \(c_0\) cell parameters with

| Brezina \textit{et al.} | \(a_0\) | 7.91 \pm 0.01 Å | 14.78 \pm 0.11 Å | 6.40 \pm 0.03 Å |
| This study | 7.894 \pm 0.003 | 14.658 \pm 0.006 | 6.401 \pm 0.003 |
| \(V=740-7\ \text{Å}^3\) | \(D_x=3.38 \ \text{g/cm}^3\) | \(Z=4\) | \(l/\text{corundum}=2.7^*\) |

\(* l/\text{corundum} \) is a reference intensity measure used by the National Bureau of Standards (Swanson, McMurtrie, Morris & Evans, 1969) and the Joint Committee on Powder Diffraction Standards. It is the ratio of the intensity of the strongest reflection in the sample [the \((221)\)' for LTT] to the intensity of the 113 reflection of corundum \((\alpha-\text{Al}_2\text{O}_3\) ).