

BRIEF COMMUNICATION

Crystal Structure Study of $(\text{Ca}, \text{Gd})_2(\text{Al}, \text{Ti})\text{O}_4$

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Received October 15, 1997; accepted March 18, 1998

The crystal structures of two crystals of $(\text{Ca}, \text{Gd})_2(\text{Al}, \text{Ti})\text{O}_4$ [tetragonal $I4/mmm$; $Z = 4$], one strongly fluorescent and the other weakly fluorescent, having minor differences in their precise compositions have been studied with single-crystal X-ray diffraction methods. The unit cell is significantly smaller for the weakly fluorescent crystal, which also shows alteration of the coordination polyhedron around the (Ca, Gd) site, suggesting the formation of vacancies at an oxygen site. © 1998 Academic Press

The title compound crystallizes in the tetragonal K_2NiF_4 -type structure (1). The Al site with traces of substituting Ti is denoted in the present work as the AT site. Approximately equal amounts of Ca and Gd atoms randomly occupy the CG site, which is coordinated by 9 oxygens, out of which $4 \times \text{O}2$ and $4 \times \text{O}1$ atoms are arranged in parallel squares rotated 45° from each other, capped by an O1 atom situated along the c -axis in the sequence [CG–O1–AT–O1–CG] within a unit cell (Fig. 1). The formation of oxygen vacancies is related with the deficiency of the AT-site atoms and the composition ratio between Ca and Gd. In view of possibilities of such applications as for laser crystals, the effect the vacancies have on the emission efficiency becomes vital.

Single crystals doped with trivalent Ti grown by the Czochralski method under a reducing atmosphere showed fluorescence decreasing in intensity with increasing amount of oxygen vacancies calculated from the analyzed composition of the cations. Details on the growth conditions and spectral measurements are reported in ref 2. Crystals showing the most and least intense fluorescence were used in this study. The color of crystal 1 is the characteristic violet indicating trivalent Ti, with the prominent fluorescence assigned to Ti^{3+} observed, while crystal 2 has a grayish-

brown coloration, showing almost no fluorescence. Both crystals were rounded into spheres with diameters of 0.10 (crystal 1) and 0.125 mm (crystal 2).

The cell constants were determined from the angular data of 25 reflections (equivalents of the 1,0,25, 2,6,14, 3,6,11, and 0,6,14 reflections; 91° – 97° in 2θ for $\text{MoK}\alpha_1$ radiation: 0.70926 \AA) with a Rigaku AFC5 automated four-circle diffractometer (40 kV, 30 mA). Intensity data were collected with $\text{MoK}\alpha$ radiation (0.7107 \AA). The structure was refined with RADY (3) after Lp and absorption corrections using fully ionized scattering factors (4, 5) and dispersion correction values (6). Weights proportional to the number of equivalents for each reflection were allotted. Restrictions for the Gram–Charlier series-expanded anharmonic parameters up to the sixth-rank tensors were taken from ref 7. Details for X-ray diffraction and structure refinement are listed in Table 1.

Refinement of the occupation parameters for only the oxygen sites gave values larger than the theoretical $1/8$ for the O2 site; therefore the occupancy for the O2 site was fixed to the theoretical value, varying the occupancies of the other sites. A decreasing tendency for all site occupancies other than the O2 site can be seen. Refined occupation parameters of cations which have systematically smaller values than full occupancy are frequently encountered in refinements with fully ionized scattering factors (8, 9), where deviations of the “observed” scattering factors with the theoretical values are believed to be reflected. As compared to crystal 1, the decrease of oxygen in crystal 2 can be seen from both the X-ray and chemical analysis results (Table 1). The values, however, exhibit margins of error similar in magnitude to the differences themselves; hence, minute compositional differences between these crystals cannot be fully ratified from these results alone. Likewise, other than the residual electron density excursions being more pronounced in crystal 2, the difference Fourier maps (Fig. 1) do not indicate any additional effects of the compositional variation.

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TABLE 1
Experimental and Refinement Conditions for the Two Crystals

	Crystal 1	Crystal 2
Analyzed composition ^a		
Temperature (K)	295	295
Ca	1.00	0.99
Gd	1.00	1.01
Al	0.98	0.94
Ti	0.01	0.004
O	3.985	3.92
Refined composition ^b		
Ca + Gd	1.93(2)	1.89(2)
Al	0.99(1)	0.97(1)
O1	1.92(3)	1.88(4)
O2	2 (fixed)	2 (fixed)
<i>a</i> (Å)	3.6617(2)	3.6607(4)
<i>c</i> (Å)	11.9888(5)	11.9865(4)
<i>D_x</i> (g/cm ³) ^c	5.780	5.680
<i>F</i> (000) ^c	250.48	246.06
μ (cm ⁻¹) ^c	216.30	211.99
Scan width: <i>a</i> + <i>b</i> tan θ in ω (deg)		
<i>a</i>	1.75	2.05
<i>b</i>	0.3	0.1
Scan speed (min ⁻¹ in ω (deg))	10	12
Maximum number of repeats	10	10
Repeated until $ F_o >$	10 $\sigma(F_o)$	10 $\sigma(F_o)$
Range of measured reflections (full reciprocal space)	0° < 2 θ < 140°	0° < 2 θ < 140°
Number of measured reflections	5992	6028
Independent (averaged) data	509	511
Used independent data with all measured equivalents observed	436	436
<i>R_{int}</i>	0.0092	0.0091
Harmonic refinement		
<i>R</i>	0.0100	0.0124
<i>R_w</i>	0.0111	0.0153
Anharmonic refinement		
<i>R</i>	0.0090	0.0110
<i>R_w</i>	0.0099	0.0137

^a The compositions were analyzed by ICP emission analysis (accurate to within a few atomic percent), the amount of oxygen being calculated from the number of cations with the formula $t = [3(q + r + s) + 2p]/2$ for the composition Ca_{1+p}Gd_{1+q}Al_{1+r}Ti_sO_{4+t}, assuming Ti to be trivalent (ref 2).

^b The number ratio for Gd:Ca is assumed to be 1:1. The AT site is assumed to be all Al. The occupation of O2 is fixed to full occupation (2.0); occupations for all other atoms are refined.

^c These values were recalculated from the refined composition.

In contrast, along with the significant shortening of distances between the sites at special positions accompanying the decrease of the cell constants, the distance between the two CG sites facing each other through the 4 × O2 basal plane shows a significant decrease in crystal 2 (Table 2). The remaining CG–O1 and AT–O1 distances in the [CG–O1–AT–O1–CG] sequence are unchanged. Conceivably, this is related to increase oxygen vacancies at the O1 site. To compensate for the loss of the lone O1-site atom situated toward its *c*-axis direction and maintain a balanced

cation coordination around the CG site, the CG atom shifts into the coordination polyhedron formed by the remaining eight oxygens. In addition, a residual accompanying the O1 site displaced along the *c*-axis direction by 0.4 Å seen in crystal 2 (Fig. 1) disappearing in the anharmonic refinement indicates that the electron density distribution of the surrounding [4 × O1] atoms is displaced along *c* in the direction opposite to the shift of the CG site. There may also be some extent of breakdown in the randomness of the distribution of Ca and Gd at the CG sites adjacent to vacancies. The lack of the characteristic coloration or fluorescence in crystal 2 may be attributed to a locally altered crystal field

TABLE 2
Refined Values for the Variable Positional Parameters (in Fractional Coordinates), Harmonic Thermal Parameters (Å²),^a and Selected Interatomic Distances (Å), with Esd's in Parentheses^b

	Crystal 1	Crystal 2
Harmonic Refinement		
AT <i>U</i> ₁₁ = <i>U</i> ₂₂	0.0033(1)	0.0034(2)
<i>U</i> ₃₃	0.0100(3)	0.0100(4)
<i>B</i> _{eq}	0.439	0.441
CG <i>z</i>	0.35857(1)	0.35863(1)
<i>U</i> ₁₁ = <i>U</i> ₂₂	0.00587(2)	0.00539(3)
<i>U</i> ₃₃	0.00491(3)	0.00465(5)
<i>B</i> _{eq}	0.438	0.405
O1 <i>z</i>	0.1677(1)	0.1677(2)
<i>U</i> ₁₁ = <i>U</i> ₂₂	0.0155(4)	0.0152(5)
<i>U</i> ₃₃	0.0060(3)	0.0055(4)
<i>B</i> _{eq}	0.971	0.942
O2 <i>U</i> ₁₁	0.0037(2)	0.0038(3)
<i>U</i> ₂₂	0.0069(3)	0.0071(4)
<i>U</i> ₃₃	0.0103(3)	0.0103(5)
<i>B</i> _{eq}	0.549	0.561
AT–O1 (× 2; <i>c</i> -axis)	2.010(1)	2.010(2)
AT–O2 (× 4)	1.8309(1)	1.8303(2)
CG–CG (<i>c</i> -axis)	3.3912(2)	3.3890(2)
CG–O1 (<i>c</i> -axis)	2.289(1)	2.289(2)
CG–O1 (× 4)	2.6082(2)	2.6076(3)
CG–O2 (× 4)	2.4954(1)	2.4943(2)
Anharmonic Refinement		
CG <i>z</i>	0.35851(4)	0.35862(5)
O1 <i>z</i>	0.1675(4)	0.1670(5)
AT–O1 (× 2; <i>c</i> -axis)	2.008(4)	2.002(6)
AT–O2 (× 4)	1.8309(1)	1.8303(2)
CG–CG (<i>c</i> -axis)	3.3926(6)	3.3894(9)
CG–O1 (<i>c</i> -axis)	2.290(4)	2.297(6)
CG–O1 (× 4)	2.6079(5)	2.6066(8)
CG–O2 (× 4)	2.4959(3)	2.4944(4)

^a The expression for the temperature factor is

$$T = \exp(-2\pi^2 \sum \sum U_{ij} h_i h_j a_i^* a_j^*), \quad B_{eq} = (8\pi^2/3) \sum \sum U_{ij} a_i^* a_j^* a_i \cdot a_j, \quad \text{and} \\ U_{eq} = B_{eq}/8\pi^2.$$

^b The harmonic thermal parameters were fixed in the anharmonic refinement to avoid correlative movements with the anharmonic parameters².

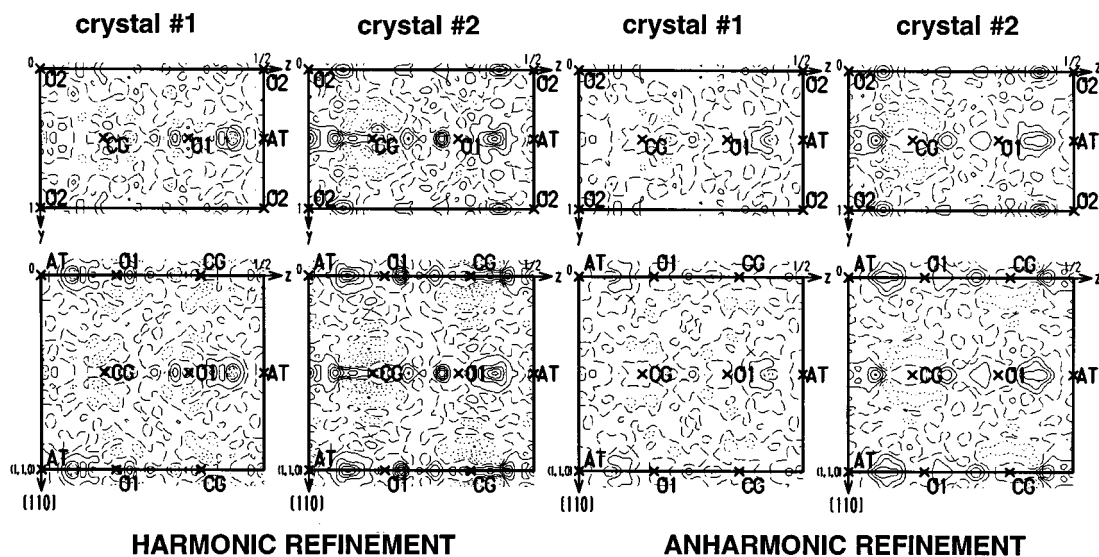


FIG. 1. Difference Fourier sections for planes $x = \frac{1}{2}$ (above) and $x = y$ (below). Positive contours are shown in full lines, zero contours in broken lines, and negative contours in dotted lines with increment $0.4 \text{ e}/\text{\AA}^3$.

around the Ti^{3+} coordination due to the partial loss of an O1 atom. These events occurring in the immediate vicinity of the oxygen vacancy and additional adjustments of the surrounding atomic positions are believed to contribute to the comparatively noisier feature seen in the difference maps for crystal 2.

The thermal parameters for the oxygens (Table 2) indicate predominantly rotational-type vibrations around the AT site.

ACKNOWLEDGMENT

All experimental measurements were made with the X-ray facilities at the Department of Geosystem Sciences, Nihon University.

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