

## Supporting Information

# Predicting the Optical Pressure Sensitivity of $^2\text{E} \rightarrow ^4\text{A}_2$ Spin-Flip Transition in $\text{Cr}^{3+}$ -doped Crystals

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**Figure S1.** XRPD pattern of  $\text{Bi}_2\text{M}_4\text{O}_9:\text{Cr}^{3+}$  ( $\text{M} = \text{Ga}, \text{Al}$ ) systems. \_\_\_\_\_ S3

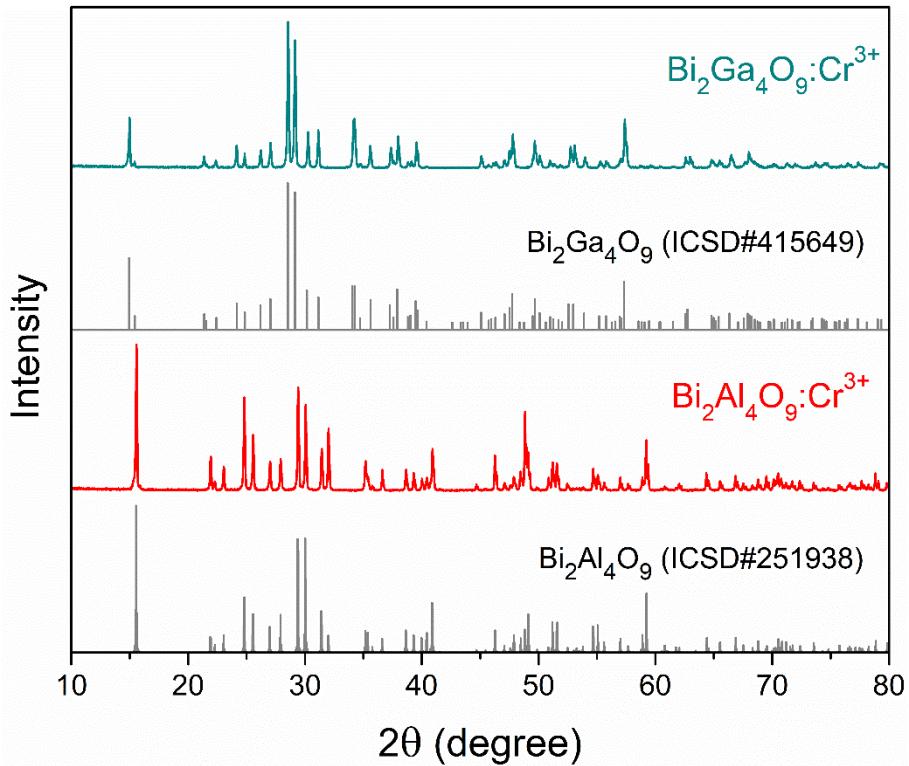
**Crystal field strength  $10Dq$  and Racah  $B$  and  $C$  parameters calculation.** \_\_\_\_\_ S3

**Table S1.** Pressure sensitivity  $\frac{d^4T_2}{dp}$  for the  ${}^4\text{T}_2 \rightarrow {}^4\text{A}_2$  transition (broadband) and bulk modulus  $B_0$  for  $\text{Cr}^{3+}$  ion in various hosts. \_\_\_\_\_ S4

**Table S2.** Pressure sensitivity  $\frac{d^2E}{dp}$  for the  ${}^2\text{E} \rightarrow {}^4\text{A}_2$  transition ( $R$ -line), crystal field strength  $Dq$ , Racah parameter  $B$  and bulk modulus  $B_0$  for  $\text{Cr}^{3+}$  ion in various hosts. \_\_\_\_\_ S4

**Figure S2.** Pressure sensitivity  $\frac{d^2E}{dp}$  for the  ${}^2\text{E} \rightarrow {}^4\text{A}_2$  transition ( $R$ -line) as a function of the (a) crystal field strength  $Dq$ , (b) the Racah parameter  $B$  and (d) the bulk modulus  $B_0$  for a variety of  $\text{Cr}^{3+}$ -doped crystals. \_\_\_\_\_ S5

**References** \_\_\_\_\_ S6



**Figure S1.** XRPD patterns of  $\text{Bi}_2\text{M}_4\text{O}_9:\text{Cr}^{3+}$  ( $\text{M} = \text{Ga}, \text{Al}$ ) systems.

### Crystal field strength $10Dq$ and Racah $B$ and $C$ parameters calculation

In the framework of Tanabe-Sugano theory, the crystal field strength  $10Dq$  and the Racah parameters  $B$  and  $C$  were calculated from the spectroscopic measurements by means of the following equations:

$$10Dq = E(^4\text{A}_2 \rightarrow ^4\text{T}_2) \quad (\text{S2})$$

$$B = \frac{\left(\Delta E_{^4\text{T}}\right)^2}{Dq} - 10\Delta E_{^4\text{T}} \quad (\text{S3})$$

$$15 \left( \frac{\Delta E_{^4\text{T}}}{Dq} - 8 \right)$$

$$C = \frac{E(^2\text{E})}{3.05} - \frac{7.9B}{3.05} + \frac{1.8}{3.08} \left( \frac{B^2}{Dq} \right) \quad (\text{S4})$$

where  $\Delta E_{^4\text{T}} = E(^4\text{T}_{1g}) - E(^4\text{T}_{2g})$  is the energy difference between the  ${}^4\text{T}_{1g}$  and  ${}^4\text{T}_{2g}$  states.

**Table S1.** Pressure sensitivity  $\frac{d^4T_2}{dp}$  for the  ${}^4T_2 \rightarrow {}^4A_2$  transition (broadband) and bulk modulus  $B_0$  for  $\text{Cr}^{3+}$  ion in various hosts.

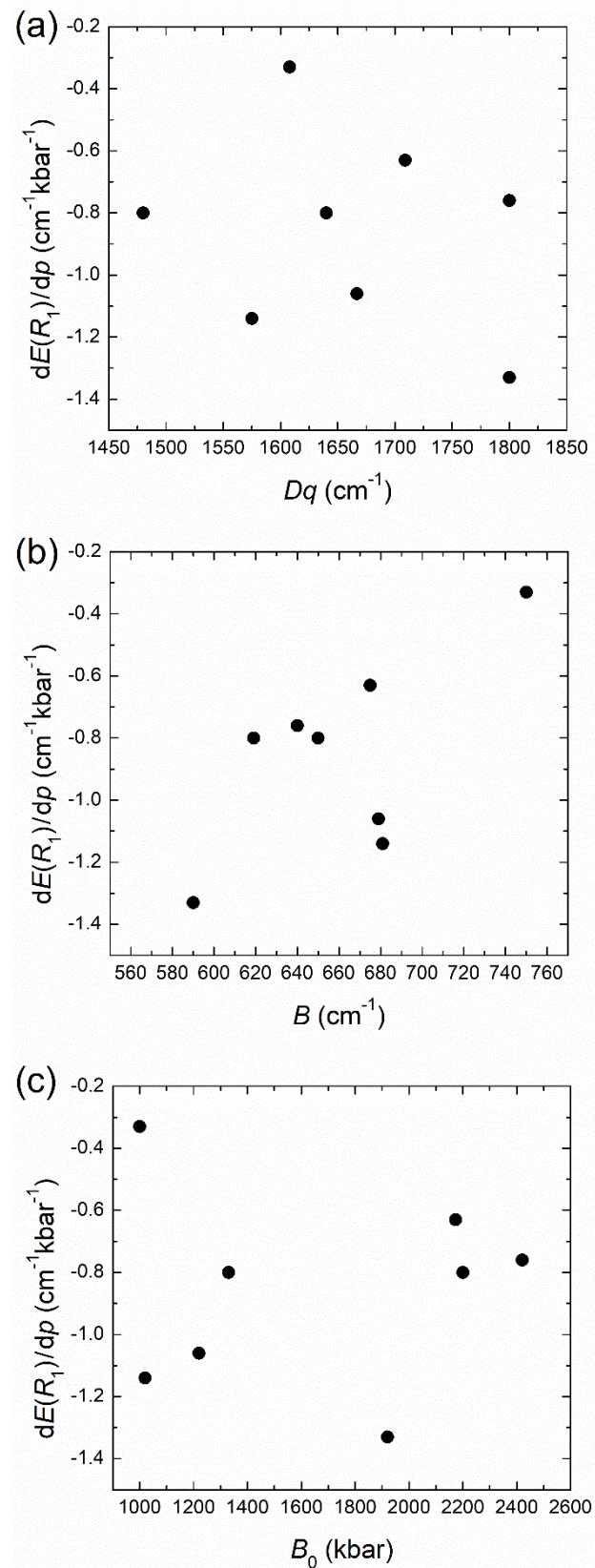
Compound	$\frac{d^4T_2}{dp}$ ( $\text{cm}^{-1}\text{kbar}^{-1}$ )	$B_0$ (kbar)	Ref.
$\text{Cs}_2\text{NaYCl}_6$	25.7	194.5	[1,2]
$\text{Cs}_2\text{NaScCl}_6$	28	231	[3,4]
$\text{K}_2\text{NaScF}_6$	17.6	453	[5,2]
$\text{K}_2\text{NaGaF}_6$	18	513	[6,2]
$\text{KZnF}_3$	17.9	776	[7,8]
$\text{LiTaO}_3$	13.5	1057	[9,10]
$\text{LiNbO}_3$	13.5	1058	[11,10]
$\text{La}_3\text{Lu}_2\text{Ga}_3\text{O}_{12}$	10	1330	[12,13]
$\text{Gd}_3\text{Ga}_5\text{O}_{12}$	10	1690	[14,15]
$\text{Y}_3\text{Al}_5\text{O}_{12}$	9	2200	[16,17]
$\alpha\text{-Al}_2\text{O}_3$ (ruby)	8.4 <sup>a</sup>	2420	[18,19]

<sup>a</sup> From absorption data.

**Table S2.** Pressure sensitivity  $\frac{d^2E}{dp}$  for the  ${}^2E \rightarrow {}^4A_2$  transition ( $R$ -line), crystal field strength  $Dq$ , Racah parameter  $B$  and bulk modulus  $B_0$  for  $\text{Cr}^{3+}$  ion in various hosts.

Compound	$\frac{d^2E}{dp}$ ( $\text{cm}^{-1}\text{kbar}^{-1}$ )	$Dq$ ( $\text{cm}^{-1}$ )	$B$ ( $\text{cm}^{-1}$ )	$B_0$ (kbar)	$E(R_1)$ ( $\text{cm}^{-1}$ )	Ref.
$\text{LiCaAlF}_6$	-0.33	1608	750	1000 <sup>a</sup>	15082.96	[20,21]
$\text{BeAl}_2\text{O}_4$	-0.63	1709	675	2173	14700.26	[22,23,24]
$\alpha\text{-Al}_2\text{O}_3$ (ruby)	-0.76	1800	650	2420	14404.66	[25,26,19]
$\text{La}_3\text{Lu}_2\text{Ga}_3\text{O}_{12}$	-0.8	1480	619	1330	14400	[12,27,13]
$\text{Y}_3\text{Al}_5\text{O}_{12}$	-0.8	1640	650	2200	14539.11	[28,26,17]
$\text{Bi}_2\text{Al}_4\text{O}_9$	-1.06	1667	679	1220	14173	This work, [29]
$\text{Bi}_2\text{Ga}_4\text{O}_9$	-1.14	1575	681	1020	14071	This work, [29]
$\text{YAlO}_3$	-1.33	1800	590	1920	13791.2	[28,30,31]

<sup>a</sup> Average value from [21].



**Figure S2.** Pressure sensitivity  $\frac{d^2E}{dp}$  for the  ${}^2\text{E} \rightarrow {}^4\text{A}_2$  transition ( $R$ -line) as a function of the (a) crystal field strength  $Dq$ , (b) the Racah parameter  $B$  and (d) the bulk modulus  $B_0$  for a variety of  $\text{Cr}^{3+}$ -doped crystals.

## References

- [1] Rienzler, A. G.; Dolan, J. F.; Kappers, L. A.; Hamilton, D. S.; Bartram, R. H. Pressure Dependence and Thermal Quenching of Chromium Photoluminescence in  $\text{Cs}_2\text{NaYCl}_6:\text{Cr}^{3+}$ . *J. Phys. Chem. Solids* **1993**, *54*, 89-100.
- [2] Sinkovits, R. S.; Bartram, R. H. Computer Modeling of Lattice Dynamics in Halide Elpasolites. *J. Phys. Chem. Solids* **1991**, *52*, 1137-1144.
- [3] Wenger, O. S.; Valiente, R.; Güdel, H. U. Influence of Hydrostatic Pressure on the Jahn-Teller Effect in the  ${}^4\text{T}_{2g}$  Excited State of  $\text{CrCl}_6^{3-}$  Doped  $\text{Cs}_2\text{NaScCl}_6$ . *J. Chem. Phys.* **2001**, *115*, 3819-3826.
- [4] Garcia-Lastra, J. M.; Moreno, M.; Barriuso, M. Pressure Effects on  $\text{CrCl}_6^{3-}$  Embedded in Cubic  $\text{Cs}_2\text{NaMCl}_6$  ( $M=\text{Sc}, \text{Y}$ ) Lattices: Study Through Periodic and Cluster Calculations. *J. Chem. Phys.* **2008**, *128*, 144708.
- [5] Dolan, J. F.; Rinzler, A. G.; Kappers, L. A.; Bartram, R. H. Pressure and Temperature Dependence of Chromium Photoluminescence Spectra in Fluoride Elpasolites. *J. Phys. Chem. Solids* **1992**, *53*, 905-912.
- [6] Dolan, J. F.; Kappers, L. A.; Bartram, R. H. Pressure and Temperature Dependence of Chromium Photoluminescence in  $\text{K}_2\text{NaGaF}_6:\text{Cr}^{3+}$ . *Phys. Rev. B* **1986**, *33*, 7339-7341.
- [7] Freire, P. T.; Pilla, O.; Lemos, V. Pressure-Induced Level Crossing in  $\text{KZnF}_3:\text{Cr}^{3+}$ . *Phys. Rev. B* **1994**, *49*, 9232-9235.
- [8] Seddik, T.; Khenata, R.; Merabiha, O.; Bouhemadou, A.; Bin-Omran, S.; Rached, D. Elastic, Electronic and Thermodynamic Properties of Fluoro-Perovskite  $\text{KZnF}_3$  via First-Principles Calculations. *Appl. Phys. A* **2012**, *106*, 645-653.
- [9] Grinberg, M.; Barzowska, J.; Shen, Y. R.; Bray, K. L. Inhomogeneous Broadening of  $\text{Cr}^{3+}$  Luminescence in Doped  $\text{LiTaO}_3$ . *Phys. Rev. B* **2001**, *63*, 214104.
- [10] Smith, R. T.; Welsh, F. S. Temperature Dependence of the Elastic, Piezoelectric, and Dielectric Constants of Lithium Tantalate and Lithium Niobate. *J. Appl. Phys.* **1971**, *42*, 2219.
- [11] Kamińska, A.; Suchocki, A.; Arizmendi, L.; Callejo, D.; Jaque, F.; Grinberg, M. Spectroscopy of Near-Stoichiometric  $\text{LiNbO}_3:\text{MgO,Cr}$  Crystals Under High Pressure. *Phys. Rev. B* **2000**, *62*, 10802-10811.
- [12] Galanciak, D.; Perlin, P.; Grinberg, M.; Suchocki, A. High Pressure Spectroscopy of LLGG Doped with  $\text{Cr}^{3+}$ . *J. Lumin.* **1994**, *60&61*, 223-226.
- [13] Wen-Chen, Z. Determination of the Local Compressibilities for  $\text{Cr}^{3+}$  Ions in Some Garnet Crystals from High-Pressure Spectroscopy. *J. Phys.: Condens. Matter* **1995**, *7*, 8351-8356.
- [14] Hömmerich, U.; Bray, K. L. High-Pressure Laser Spectroscopy of  $\text{Cr}^{3+}:\text{Gd}_3\text{Sc}_2\text{Ga}_3\text{O}_{12}$  and  $\text{Cr}^{3+}:\text{Gd}_3\text{Ga}_5\text{O}_{12}$ . *Phys. Rev. B* **1995**, *51*, 12133-12141.
- [15] Durygin, A.; Drozd, V.; Paszkowicz, W.; Werner-Malento, E.; Buczko, R.; Kaminska, A.; Saxena, S.; Suchocki, A. Equation of State for Gadolinium Gallium Garnet Crystals: Experimental and Computational Study. *Appl. Phys. Lett.* **2009**, *95*, 141902.

- [16] Wamsley, P. R.; Bray, K. L. The Effect of Pressure on the Luminescence of Cr<sup>3+</sup>:YAG. *J. Lumin.* **1994**, *59*, 11-17.
- [17] Xu, Y.-N.; Ching, W. Y. Electronic Structure of Yttrium Aluminum Garnet (Y<sub>3</sub>Al<sub>5</sub>O<sub>12</sub>). *Phys. Rev. B* **1999**, *59*, 10530-10535.
- [18] Duclos, S. J.; Vohra, Y. K.; Ruoff, A. L. Pressure Dependence of the <sup>4</sup>T<sub>2</sub> and <sup>4</sup>T<sub>1</sub> Absorption Bands of Ruby to 35 GPa. *Phys. Rev. B* **1990**, *41*, 5372-5381.
- [19] Kim-Zajonz, J.; Werner, S.; Schulz, H. High Pressure Single Crystal X-ray Diffraction Study on Ruby up to 31 GPa. *Z. Kristallogr.* **1999**, *214*, 331-336.
- [20] Sanz-Ortiz, M. N.; Rodriguez, F.; Hernandez, I.; Valiente, R.; Kück, S. Origin of the <sup>2</sup>E↔<sup>4</sup>T<sub>2</sub> Fano Resonance in Cr<sup>3+</sup>-Doped LiCaAlF<sub>6</sub>: Pressure-Induced Excited-State Crossover. *Phys. Rev. B* **2010**, *81*, 045114.
- [21] Shimizu, T. et al. High Pressure Band Gap Modification of LiCaAlF<sub>6</sub>. *Appl. Phys. Lett.* **2017**, *110*, 141902.
- [22] Jahren, A. H.; Kruger, M. B.; Jeanloz, R. Alexandrite as a High-Temperature Pressure Calibrant, and Implications for the Ruby-Fluorescence Scale. *J. Appl. Phys.* **1992**, *71*, 1579-1582.
- [23] Suchocki, A. B.; Gilliland, G. D.; Powell, R. C.; Bowen, J. M.; Walling, J. C. Spectroscopic Properties of Alexandrite Crystals II. *J. Lumin.* **1987**, *37*, 29-37.
- [24] Ching, W. Y.; Xu, Y.-N.; Brickeen, B. K. Comparative Study of the Electronic Structure of Two Laser Crystals: BeAl<sub>2</sub>O<sub>4</sub> and LiYF<sub>4</sub>. *Phys. Rev. B* **2001**, *63*, 115101.
- [25] Forman, R. A.; Piermarini, G. J.; Barnett, J. D.; Block, S. Pressure Measurement Made by the Utilization of Ruby Sharp-Line Luminescence. *Science* **1972**, *176*, 284-285.
- [26] Wood, D. L.; Ferguson, J.; Knox, K.; Dillon, J. F. Crystal-Field Spectra of d<sup>3,7</sup> Ions. III. Spectrum of Cr<sup>3+</sup> in Various Octahedral Crystal Fields. *J. Chem. Phys.* **1963**, *39*, 890-898.
- [27] Struve, B.; Huber, G. The Effect of the Crystal Field Strength on the Optical Spectra of Cr<sup>3+</sup> in Gallium Garnet Laser Crystals. *Appl. Phys. B* **1985**, *36*, 195-201.
- [28] Barnett, J. D.; Block, S.; Piermarini, G. J. An Optical Fluorescence System for Quantitative Pressure Measurement in the Diamond Anvil Cell. *Rev. Sci. Instrum.* **1973**, *44*, 1-9.
- [29] Lopez-de-la-Torre, L.; Friedrich, A.; Juarez-Arellano, E. A.; Winkler, B.; Wilson, D. J.; Bayarjargal, L.; Hanfland, M.; Burianek, M.; Mühlberg, M.; Schneider, H. High-Pressure Behavior of the Ternary Bismuth Oxides Bi<sub>2</sub>Al<sub>4</sub>O<sub>9</sub>, Bi<sub>2</sub>Ga<sub>4</sub>O<sub>9</sub> and Bi<sub>2</sub>Mn<sub>4</sub>O<sub>10</sub>. *J. Solid State Chem.* **2009**, *182*, 767-777.
- [30] Weber, M. J.; Varitimos, T. E. Optical Spectra and Relaxation of Cr<sup>3+</sup> Ions in YAlO<sub>3</sub>. *J. Appl. Phys.* **1974**, *45*, 810-816.
- [31] Ross, N. L.; Zhao, J.; Angel, R. J. High-Pressure Single-Crystal X-ray Diffraction Study of YAlO<sub>3</sub> Perovskite. *J. Solid State Chem.* **2004**, *177*, 1276-1284.