

Crystal structure of the group of optical materials $\text{Ln}_2\text{MeGe}_4\text{O}_{12}$ (Me = Ca, Mn)

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Abstract. The crystal structure of the group of optical materials $\text{Ln}_2\text{MeGe}_4\text{O}_{12}$, Ln = Eu, Gd, Dy-Lu, Y; Me = Ca, Mn and of the solid solution $(\text{Y}_{1-x}\text{Er}_x)_2\text{CaGe}_4\text{O}_{12}$ ($x = 0 - 1$), promising materials for photonics, has been studied in detail. The crystal structure of all compounds exhibit two alternating layers: one formed by Ln and Me atoms and another by cyclic $[\text{Ge}_4\text{O}_{12}]^{8-}$ anions.

Introduction

One of the well-known problems of modern photonics is the practical use of the far- and mid-IR ranges. Therefore synthesis of new compounds allowing up- and down emission conversion is one of the main goals of materials science. Recently, it was found that the new group of optical materials $\text{Ln}_2\text{CaGe}_4\text{O}_{12}$, Ln = Gd, Ho, Er, Yb and Y ($\Delta E = 4.95(5)\text{eV}$) shows luminescence under continuous laser pumping at $\lambda = 976\text{ nm}$ [1-3]. The crystal structure and the optical and luminescence properties of these rare-earth tetrametagermanates were discussed earlier [2-5]. This work concentrates on crystal structure features of the concerned compounds and takes into consideration a broader range of germanates, $\text{Ln}_2\text{MeGe}_4\text{O}_{12}$, Ln = Eu, Gd, Dy-Lu, Y; Me = Ca, Mn and the solid solution $(\text{Y}_{1-x}\text{Er}_x)_2\text{CaGe}_4\text{O}_{12}$ ($x = 0 - 1$).

Experiment

The $\text{Ln}_2\text{MeGe}_4\text{O}_{12}$, Ln = Eu, Gd, Dy-Lu, Y; Me = Ca, Mn samples and the $(\text{Y}_{1-x}\text{Er}_x)_2\text{CaGe}_4\text{O}_{12}$ ($x = 0 - 1$) solid solution were prepared by solid-state reaction in air from stoichiometric mixtures of Ln_2O_3 (Ln = Eu, Gd, Dy, Ho, Er, Tm, Yb, Lu, Y), $\text{CaCO}_3(99.9\%)$, $\text{Mn}_2\text{O}_3(99.9\%)$ and $\text{GeO}_2(99.9\%)$ at $T = 1100^\circ\text{C}$ as described in [1].

X-ray powder diffraction (XRD) patterns were collected at room temperature on a transmission STADI-P (STOE, Germany) diffractometer equipped with a linear mini-PSD detector, using Cu $K\alpha_1$ radiation in the 2θ range 2° to 120° with a step of 0.02° . Polycrystalline silicon ($a = 5.43075(5)$ Å) was used as external standard. The phase purity of the samples was checked by comparing their XRD patterns with those in the Powder diffraction file - PDF2 database (ICDD, USA, release 2007). The crystal structure has been refined with the GSAS [6] program suite using X-ray powder diffraction data.

For the transmission electron microscopy (TEM) studies the samples were crushed in ethanol. A drop of this suspension was put on a copper grid covered with a holey carbon film.

The energy dispersive X-ray (EDX) spectra and electron diffraction (ED) patterns were obtained using a Philips CM20 operated at 200 kV, equipped with an Oxford INCA system.

Results and discussion

The XRD and ED patterns have been indexed in the S.G. $P4/nbm$ (N. 125), $Z = 2$. Selected area diffraction patterns viewed along the $[100]$ and $[001]$ zone axes and the XRD pattern are shown in figure 1. EDX analyses of all compounds were made to check the purity of the samples. The obtained compositions were in good agreement with the nominal compositions.

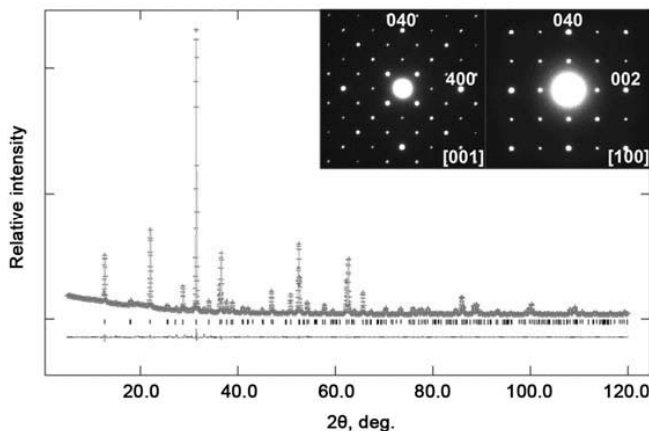


Figure 1. Observed (crosses), calculated (solid line) and difference (bottom) powder diffraction pattern of $\text{Ho}_2\text{CaGe}_4\text{O}_{12}$ ($\text{Ln}_2\text{MeGe}_4\text{O}_{12}$, $\text{Ln} = \text{Eu, Gd, Dy-Lu}$, Y ; $\text{Me} = \text{Ca, Mn}$). Inset: Selected area electron diffraction patterns of concerned germanates recorded along $[001]^*$ and $[100]^*$.

The variation in the unit cell parameters of the $\text{Ln}_2\text{MeGe}_4\text{O}_{12}$, $\text{Ln} = \text{Eu, Gd, Dy-Lu, Y}$; $\text{Me} = \text{Ca, Mn}$ for the different rare-earth elements is shown in the figure 2 (b). The structure of $\text{Y}_2\text{CaGe}_4\text{O}_{12}$ [1] was used as starting model for the crystal structure refinement. The peak profiles were fitted with a pseudo-Voigt function, $I(2\theta) = x \cdot L(2\theta) + (1-x) \cdot G(2\theta)$ (where L and G are the Lorentzian and Gaussian part, respectively). The angular dependence of the peak width was described by the relation $(FWHM)^2 = U \tan^2\theta + V \tan\theta + W$, where $FWHM$ is the full line width at half maximum. The background level was described as a combination

of fifteenth Chebyshev polynomials. In total, 49 parameters for each pattern were refined. The complete details of the refinement, refined atomic coordinates, temperature parameters and R-values are given in [2, 3]. The crystal structure of the $\text{Ln}_2\text{MeGe}_4\text{O}_{12}$, $\text{Ln} = \text{Eu, Gd, Dy-Lu, Y}$; $\text{Me} = \text{Ca, Mn}$ can be described as consisting of alternating layers of cations and tetrahedra $[\text{Ge}_4\text{O}_{12}]$ (figure 3). Calcium, manganese and Ln atoms are located at the octahedral $4f$ site $(0, 0, \frac{1}{2})$ in a 0.5/0.5 ratio; the $2b$ site $(\frac{1}{4}, \frac{1}{4}, \frac{1}{2})$ is fully occupied with Ln atoms. An attempt to refine the occupancy of the Ln sites showed that within standard deviation the $\text{Ca}(\text{Mn})/\text{Ln}$ occupancy of the $4f$ position is equal to 0.5/0.5 for all concerned compounds.

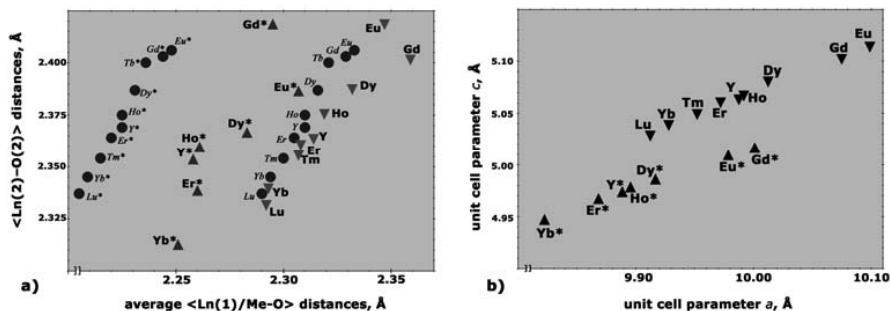


Figure 2. a) Correlation between average distances in octahedral ($\text{Ln}(1)/\text{Me}-\text{O}$) and antiprism ($\text{Ln}(2)-\text{O}(2)$): black circles – theoretical values for $\text{Ln}_2\text{CaGe}_4\text{O}_{12}$, $\text{Ln} = \text{Eu, Gd, Dy-Lu, Y}$; with * - note for manganese compounds [11]; grey triangles – experimental value for $\text{Ln}_2\text{CaGe}_4\text{O}_{12}$, $\text{Ln} = \text{Eu, Gd, Dy-Lu, Y}$; with * - note for manganese compounds; b) The variation of unit cell parameters of the $\text{Ln}_2\text{MeGe}_4\text{O}_{12}$, $\text{Ln} = \text{Eu, Gd, Dy-Lu, Y}$; $\text{Me} = \text{Ca, Mn}$ for the different rare-earth elements (upturned triangles - for calcium compounds; triangles with * note - for manganese compounds).

The octahedra occupied by Ln and $\text{Ca}(\text{Mn})$ atoms are elongated along the distances to the $\text{O}(1)$ atoms and shortened along the distances to the $\text{O}(2)$ atoms. This is a specific feature of this type of structure [1-5, 7-12]. The average $\text{Ln}(1)/\text{Ca}(\text{Mn})-\text{O}$ distances in octahedra and the $\text{Ln}(2)-\text{O}(2)$ distances in square antiprisms are shortened with decreasing of the crystal radii of the rare-earth element, figure 2a. However, a linear dependence is not strict for cations with bigger crystal radius. For example, substitution of Gd ($r(\text{Gd}^{3+})=1.078 \text{ Å}$) [13] allows stabilization of the $\text{Gd}_2\text{Ca}(\text{GeO}_3)_4$ structure; however, the octahedra are heavily distorted. Attempts to obtain $\text{Nd}_2\text{Ca}(\text{GeO}_3)_4$ were not successful at all probably due to the relatively big size of Nd atoms ($r(\text{Nd}^{3+})=1.123 \text{ Å}$). As an indirect evidence to prove it, the existence of the $\text{CeMn}_2\text{Ge}_4\text{O}_{12}$ compound, in which Mn atoms occupy only the octahedral $4f$ site while Ce^{4+} atoms ($r(\text{Ce}^{4+})=1.11 \text{ Å}$) occupy only $2b$ site can be considered [4].

Germanium atoms are located at the tetrahedral $8k$ site $(x/a, \frac{1}{4}, 0)$. The difference between the $\text{Ge}-\text{O}(1)$ and $\text{Ge}-\text{O}(2)$ bond lengths in GeO_4 tetrahedra ranges from 0.055 Å (for Y/Ca) to 0.086 Å (for Gd/Ca). In [5] and [14] it has been shown that Ge_4O_{12} groups in cyclogermanates consist of $\text{O}(2)\text{GeO}(2)$ groups which are connected to each other by means of $\text{Ge}-\text{O}(1)-\text{Ge}$ bridge bonds. For all compounds the germanium tetracycle is considerably distorted and rigid; the bond angles for the $\text{O}(2)\text{GeO}(2)$ groups vary from 121.0 to 122.5° and for the $\text{Ge}-\text{O}(1)-\text{Ge}$ from 126.5 to 127.5° . The distortion is associated with the $\text{O}(2)-\text{O}(2)$ distances,

which form the local environment of a Ln atom in a square antiprism. For calcium compounds, as the Ln radius decreases, both the Ln–O(2) distances and the lengths of the O(2)–O(2) edges of the square antiprism decrease. The length of the edge lying in the *ab* plane in $\text{Yb}_2\text{Ca}(\text{GeO}_3)_4$ (2.82 Å) and $\text{Lu}_2\text{Ca}(\text{GeO}_3)_4$ (2.81 Å) is exactly equal to the sum of the crystal

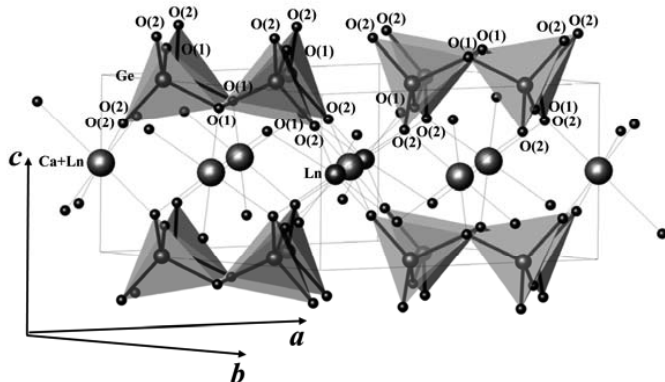


Figure 3. Crystal structure of $\text{Ln}_2\text{MeGe}_4\text{O}_{12}$, Ln = Eu, Gd, Dy-Lu, Y; Me = Ca, Mn.

radii of two oxygen atoms. This means that the four O(2) atoms which form the face of the square antiprism in the *ab* plane are in close contact. Thus, the tetracycles in $\text{Ln}_2\text{Ca}(\text{GeO}_3)_4$ (Ln = Gd, Ho, Er, Y, Dy, Tm) can be considered as isolated and rigid, whereas in $\text{Yb}_2\text{Ca}(\text{GeO}_3)_4$ and $\text{Lu}_2\text{Ca}(\text{GeO}_3)_4$ they form two-dimensional networks.

A similar behavior is observed for the manganese cyclogermanates, but with some particular features caused by a smaller radius of Mn^{2+} ($r(\text{VI})=0.97$ Å). First of all they display a heavier distortion of the octahedra and a large deviation of the *c/a* parameter from 1 (figure 2b).

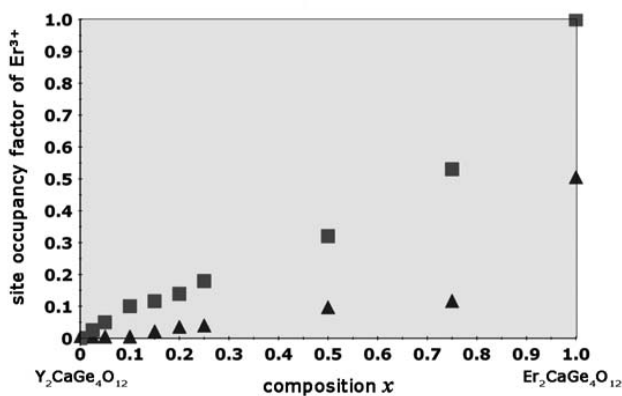


Figure 4. Dependence of site occupancies of Er^{3+} on composition *x* (*x* = 0 - 1) for the $\text{Er}_x\text{Y}_{2-x}\text{CaGe}_4\text{O}_{12}$ solid solution (triangles – six-coordinated site; squares – eight-coordinated site).

Meanwhile the tendency in the change of the O(2)–O(2) distances remains the same as for calcium tetragermanates; the germanium tetracycle is considerably distorted and rigid. Only in case of $\text{Yb}_2\text{Mn}(\text{GeO}_3)_4$ the formation of two-dimensional networks was observed.

In order to determine a tendency according to which rare earth elements occupy six- or eight-coordinated sites in the structure the solid solution $\text{Er}_x\text{Y}_{2-x}\text{CaGe}_4\text{O}_{12}$ was first synthesized. A smooth change of the unit cell parameters and volume with x has been observed in the whole range of solid solution. The refinement procedure reveals that Er atoms mainly occupy the $2b$ sites with antiprismatic configuration and less the octahedral $4f$ site (figure 4).

Thus, the crystal structure of the $\text{Ln}_2\text{MeGe}_4\text{O}_{12}$, $\text{Ln} = \text{Eu, Gd, Dy-Lu, Y}$; $\text{Me} = \text{Ca, Mn}$, which can be considered as a two-sublattice system composed of polyatomic anions (tetracycles $[\text{Ge}_4\text{O}_{12}]^{8-}$) weakly bound to each other and a “heavy” cationic sublattice, determines their optical properties.

Concluding remarks

A group of optical materials $\text{Ln}_2\text{MeGe}_4\text{O}_{12}$, $\text{Ln} = \text{Eu, Gd, Dy-Lu, Y}$; $\text{Me} = \text{Ca, Mn}$ and the solid solution $(\text{Y}_{1-x}\text{Er}_x)_2\text{CaGe}_4\text{O}_{12}$ with $x = 0 - 1$ have been synthesized and their crystal structure studied in detail. An isovalent substitution of cations in the two-sublattice crystal structure allows the tuning of optical properties. The synthesis of the isostructural series of manganese-containing compounds $\text{Ln}_2\text{MnGe}_4\text{O}_{12}$, $\text{Ln} = \text{Eu, Gd, Dy, Ho, Er, Yb, Y}$ allows revealing new structural features of tetragermanates and also the extension of the total number of promising optical matrices containing $[\text{Ge}_4\text{O}_{12}]^{8-}$ groups.

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