

In_{1.08}Gd_{0.92}Ge₂O₇: a new member of the thortveitite family

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Indium gadolinium digermanium heptaoxide, In_{1.08}Gd_{0.92}Ge₂O₇, with a thortveitite-type structure, has been prepared as a polycrystalline powder material by a high-temperature solid-state reaction. As in the mineral thortveitite, the crystal structure belongs to the monoclinic system, with space group *C2/m* (No. 12). The precise structural parameters were obtained by applying the Rietveld method of refinement to the X-ray powder diffraction data. This layered structure presents, on one side, a honeycomb-like arrangement of the unique octahedral site, which is occupied randomly by In and Gd atoms, and, on the other side, sheets of isolated Ge₂O₇ diortho-groups made up of double tetrahedra sharing a common vertex and displaying *C_{2h}* point symmetry. This compound showed a remarkable photoluminescence effect when it was irradiated with the X-ray beam during the X-ray diffraction measurements, and with the α beam during the Rutherford back-scattering spectrometry experiments employed to analyze the chemical stoichiometry.

Comment

Since Zachariassen (1930) published his work on the Sc₂Si₂O₇ thortveitite structure, many compounds belonging to this structure type have been synthesized and their complete and precise structural data reported. In 1962, as a result of a reinvestigation of the crystal structure of thortveitite, Cruickshank *et al.* (1962) considered the possibility of exchanging Sc³⁺ with other cations, such as Y³⁺ and Fe³⁺, to observe the effects that this might have on the crystal symmetry, specifically on the point symmetry shown by the Ge₂O₇ diortho-group and the presence or otherwise of a mirror plane, which is the difference between *C2* and *C2/m* as possible space groups for thortveitite.

In subsequent years, many compounds have been synthesized which presented the thortveitite structure or variations of it, namely Sm₂Si₂O₇ (Smolin *et al.*, 1970), Y₂Si₂O₇ (Batalieva & Pyatenko, 1971), Pr₂Si₂O₇ (Felshe, 1971), In₂Si₂O₇ (Reid *et al.*, 1977; Gaewdang *et al.*, 1994) and Gd₂Si₂O₇

(Smolin & Shepelev, 1967). In the same way, the Si atom has been exchanged for Ge, giving rise to the pyrogermanate compounds Er₂Ge₂O₇ (Smolin, 1970), Gd₂Ge₂O₇ (Smolin *et al.*, 1971), Eu₂Ge₂O₇ (Chigarov *et al.*, 1983) and so on. Many of these germanium-based compounds also retained the thortveitite structure, but some of them changed their crystal symmetry.

Recently, the crystal structure of iron indium digermanate, FeInGe₂O₇, has been reported (Bucio *et al.*, 2001), which also has the typical thortveitite layered structure. This compound belongs to a new class of monoclinic germanates, of general stoichiometric formula *M*RGe₂O₇, where *M* and *R* represent trivalent metals (such as Al, Ga or Fe) and rare earth ions, respectively. Among these compounds can be found crystal symmetries described by the space groups *C2/m* (No. 12), as in thortveitite, *C2/c* (No. 15), represented by InTbGe₂O₇ (Juarez-Arellano *et al.*, 2002), *P2₁/c* (No. 14), as in FeRGe₂O₇ (*R* is La, Pr, Nd or Gd; Bucio *et al.*, 1996), and *P2₁/m* (No. 11), as in FeRGe₂O₇ (*R* is Y or Tb/Yb; Cascales *et al.*, 1998).

This kind of compound has been of great interest in laser crystal physics. For instance, the incorporation of R³⁺ activators into single-centred hosts, up to full substitution of all cations, gives the possibility of obtaining so-called self-activated crystals. Other recently reported layered compounds with interesting optical responses are GdMnGe₂O₇ (Taviot-Gueho *et al.*, 1999) and MnEuGe₂O₇ (Juarez-Arellano *et al.*, 2001), these being the only cases in which an orthorhombic symmetry (space group *A222*, No. 21) can be found.

In recent years, compounds with rare earth cations, especially Gd³⁺, have been developed and employed as scintillators for applications in a variety of fields, such as medical imaging, high-energy physics and space-borne γ -ray astronomy (Moses *et al.*, 1997; Yasunobu *et al.*, 2001). The present work is devoted to the synthesis and crystal structure characterization of a new gadolinium-based compound having the formula

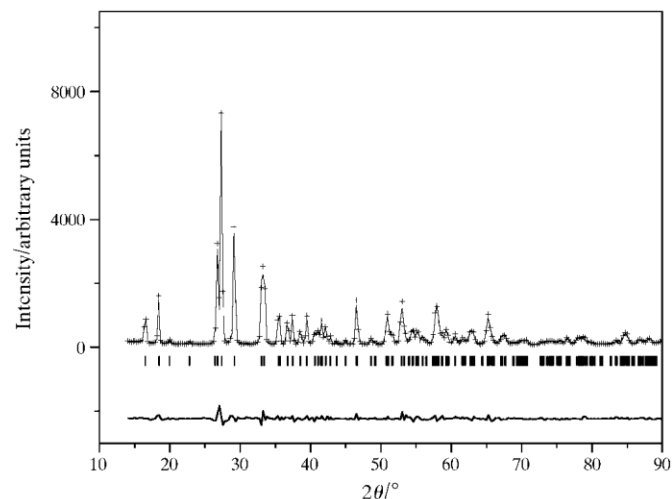


Figure 1

The observed (+++) and calculated (solid line) X-ray powder diffraction profiles for In_{1.08}Gd_{0.92}Ge₂O₇ at room temperature. The difference profile is given at the bottom. The vertical marks correspond to the positions of the allowed Bragg reflections.