

The crystal structure of $\text{FeInGe}_2\text{O}_7$

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Abstract. A new iron indium germanate has been prepared as polycrystalline powder material which crystallizes in the monoclinic system (S.G. $C2/m$, No. 12). The structure was characterized by X-ray powder diffraction and Rietveld refinement of the resulting diffraction pattern. The cell parameters are $a = 6.5124(4) \text{ \AA}$, $b = 8.5914(5) \text{ \AA}$, $c = 4.8936(3) \text{ \AA}$, $\beta = 102.683(2)^\circ$, $V = 267.12(3) \text{ \AA}^3$ and $Z = 2$. The structure contains R^{+3} cations ($R = \text{Fe, In}$) almost equally distributed in distorted RO_6 octahedral sites. These octahedra are joined by edge sharing forming a hexagonal arrangement on the ab planes. The RO_6 octahedra layers are held together by sheets of isolated Ge_2O_7 diorthogroups constituted by a double tetrahedra sharing a common vertex. This compound has the thortveitite structure and keeps a strong relationship with the FeYGe_2O_7 germanate, which presents two R^{+3} sites with six-coordinated ($R = \text{Fe}$) and seven-coordinated ($R = \text{Y}$) oxygens, corresponding to the different symmetry given by the monoclinic space group $P2_1/m$ (No. 11).

Introduction

The family of germanates MRGe_2O_7 , in which M and R represent trivalent metals, Al, Ga or Fe, and rare earth ions respectively, supplies a class of single-centered compounds, which have been of great interest in laser crystal physics, for instance, the incorporation of R^{+3} activators into single-centered hosts up to full substitution of all cations gives the possibility to obtain the so-called self-activated crystals. The spectroscopic study of series of such compounds supplies much valuable information for the crystal field theory of R^{+3} ions and for understanding numerous applied optical effects. For the indium pyrogermanate $\text{In}_2\text{Ge}_2\text{O}_7$ and pyrosilicate $\text{In}_2\text{Si}_2\text{O}_7$, luminescence properties below 160 and 200 K respectively were reported. It was shown that the luminescence is due to the presence of In^{3+} having the $4d^{10}$ electronic configuration [1]. On the other hand, detailed studies about absorption, luminescence and stimulated emission, were carried out in the $\text{AlNdGe}_2\text{O}_7$ compound [2], which crystallizes in the monoclinic system with space group $P2_1/c$ (No. 14) and $Z = 4$. In the iron family of germanates FeRGe_2O_7 , depending on the size of R, three crystal structure types can

be found. The type I for $R = \text{La to Gd}$ having the $\text{AlNdGe}_2\text{O}_7$ crystal structure [3–4]; the type II for $R = \text{Y, Tb–Yb}$, with space group $P2_1/m$ (No. 11) [5, 6], and type III for $R = \text{In and Sc}$, which structure determination is the subject of the present paper. In order to investigate more carefully the optical properties in the type III family of germanates; the present work is devoted to the precise crystal structure characterization of the $\text{FeInGe}_2\text{O}_7$ compound.

Experimental

Sample preparation

$\text{FeInGe}_2\text{O}_7$ was prepared as polycrystalline powder material by solid state reaction from stoichiometric mixtures of analytical grade Fe_3O_4 , GeO_2 and In_2O_3 . The sample was ground and heated in air at 1150°C for 5 days with intermediate regrindings. The standard x-ray powder diffraction analysis indicated that the final sample was well crystallized and appeared completely free of mixture crystalline phases.

Chemical composition

Because some of GeO_2 could be lost after the thermal treatment, especially as vitrified product, it was necessary to establish unambiguously the correct stoichiometric formula for the new synthesized compound. The elemental composition was measured by Rutherford Backscattering Spectroscopy (RBS) [7]. The sample was previously well powdered and pressed in small pellet. This pellet was irradiated in vacuum using a 2.5 MeV proton beam (1 mm diameter). A Canberra PIPS detector (Passivated Implanted Planar Silicon detector) was placed at 168° from the beam direction to collect backscattered particles for RBS spectra. RUMP code [8, 9] was used to simulate RBS spectra in order to determine the elemental composition given by $\text{Fe} = 1.03(5)$, $\text{In} = 1.00(5)$, $\text{Ge} = 2.02(5)$ and $\text{O} = 7.3(5)$.

X-ray diffraction analysis

X-ray powder diffraction pattern was recorded at room-temperature with a step size of 0.02° over $10\text{--}120^\circ 2\theta$ -range. The diffraction data were collected with a counting time of 10s each step using a Siemens D5000 Dif-

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