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Space formations and nonlinear properties of noncentrosymmetric germanates

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ABSTRACT

Space formations of Ge–O polyhedra have been analyzed for 114 noncentrosymmetric germanates. The type of Ge–O polyhedra space formations is dependent on the stoichiometric ratio SR=n(O)/n(Ge), where n(O) is the number of oxygen and n(Ge) is the number of germanium atoms in formal composition of the compound. Individual (Ge–O) polyhedra are found for SR ≥ 3 chains of the polyhedra that exist in the range of SR=3–5. Only framework formations are possible at SR ≤ 2.7.

1. Introduction

Germanate crystals are among the basic materials of modern electronics, optics, acoustic electronics, optoelectronics, laser physics and second harmonic generation [1–9]. Therefore, searching for new germanate materials with high materials properties is evidently topical. In inorganic materials, crystal macroscopic nonlinearity is the geometrical superposition of the microscopic SHG-active anionic units. Therefore, such kinds of SHG-active units have attracted more and more attention. As is believed, specific features of Ge–O polyhedra space arrangement and the formation of covalent oxide bonds with sufficient electronic polarizability are among the factors essential for compounds of optical nonlinearity. Structurally, for any particular oxide lattice element *El*, such as *El*–O, polyhedra arrangements can be considered as isolated (simple) zero-dimensional (0D), one-dimensional (chains) (1D), two-dimensional (layers) (2D) and three-dimensional (frames) (3D). Here, in the 0D formation, the *El*–O polyhedra are individual and bonds like *El*–O–*El* are absent in the crystal lattice (Fig. 1). When the 1D formation appears, *El*–O polyhedra are linked in any dominant direction by –O–*El*–O–*El*–O– constructions with the formation of infinite chains (Fig. 2). Furthermore, in 2D- and 3D-formations, the –O–*El*–O–*El*–O– constructions occur in two and three dimensions, respectively, providing the layers and frames formation (Fig. 3). Even this simple classification of the crystals reveals the presence of particular directions in the crystal framework; for example the direction along the chains in 1D formation or the direction perpendicular to a layer plane in 2D formation. So, if high crystal optical nonlinearity observed for germanates was governed by high polarizability of distorted Ge–O polyhedra, then the existence of these particular directions of polyhedra arrangement and volume concentration of the polyhedra would influence principally the optical nonlinearity of the crystal. This hypothesis may be tested by direct correlation of the reported nonlinear optical coefficients with Ge–O polyhedra packaging evaluated for germanate compounds for which the

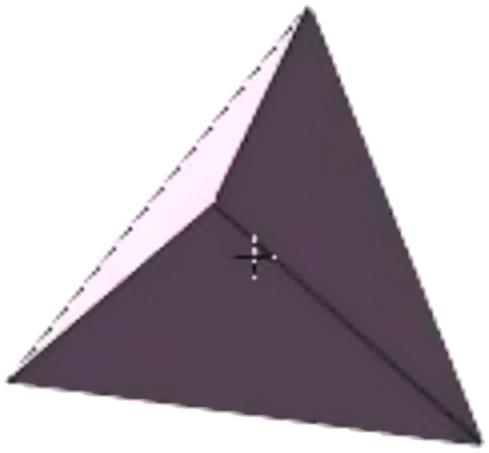

Fig. 1. Simple 0D formation of GeO_4 ($LiBGeO_4$).

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crystal structure is specified. So, this study is aimed at defining the quantitative criteria for different Ge–O polyhedra formations in noncentrosymmetrical Ge oxide crystals.

2. Classification and parameters

Searching for published results on the crystal structure of noncentrosymmetric germanate crystals gives a collection of 114 crystals. Only the crystals not having halogenides, chalcogenides, hydrogen, nitrogen and carbon, and the structure which has been defined with $R < 15\%$ were selected. The distribution of the compounds over the symmetry and space formations of Ge–O polyhedra is shown in Table 1. To describe the space formation of Ge–O polyhedra, stoichiometric ratio $SR = n(O)/n(Ge)$ is used as a quantitative criterion. Mathematically, parameter SR is equal to the ratio between the total number of oxygen atoms in the stoichiometric formula and the number of germanium atoms. So,

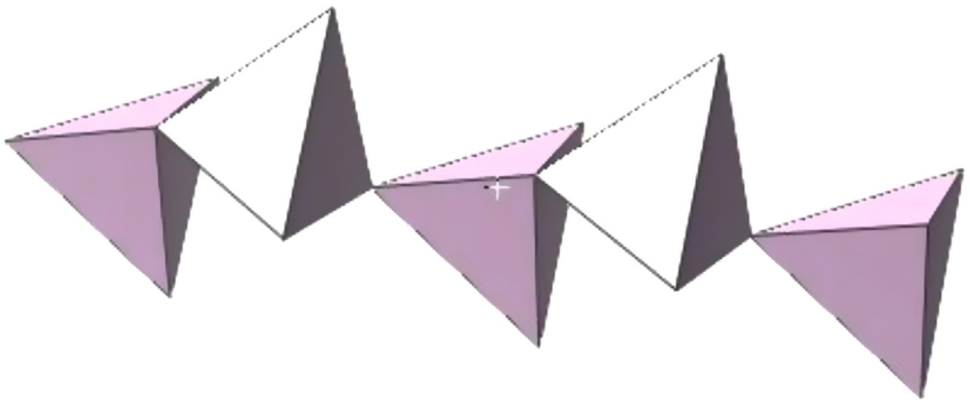

Fig. 2. Chain 1D formation of GeO_4 (Na_2GeO_3).

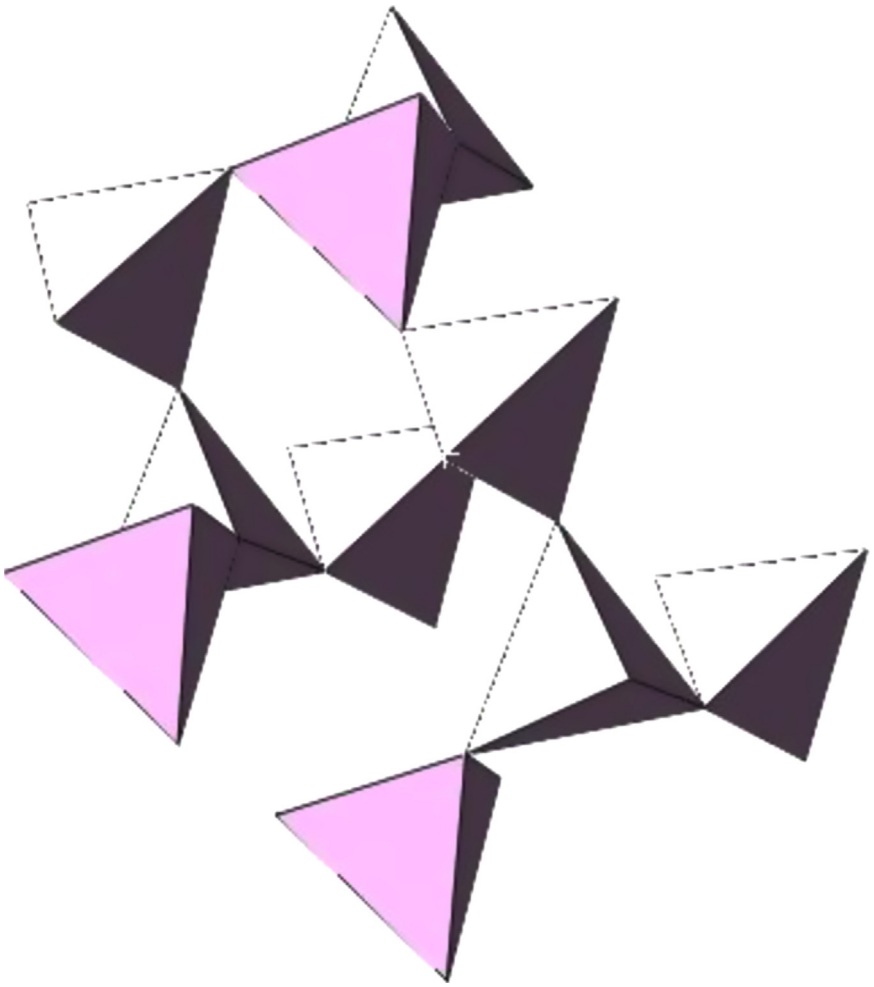

Fig. 3. Framework 3D formation of GeO_4 (GeO_2).