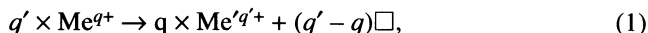


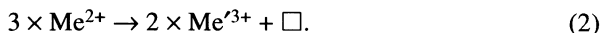
## Heterovalent Vacancy-Coupled Substitution

We here consider the case in which the cations  $\text{Me}^{q+}$  with formal charge  $q+$  of a parent crystal are replaced by other cations  $\text{Me}'^{q'+}$  with formal charge  $q'+$ , where  $q' > q$ . To attain charge neutrality through such a heterovalent replacement,  $q' \times \text{Me}'^{q'+}$  cations are replaced every  $q \times \text{Me}^{q+}$ , leaving  $(q' - q)$  crystallographic vacancies per  $q \times \text{Me}^{q+}$  in the crystal. This situation may be expressed by



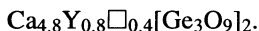
where the square denotes a vacancy.

For the present purpose, such a replacement is specifically confined to the case in which  $q = 2$  and  $q' = 3$ . Therefore, the above relation is rewritten by



Now, suppose that crystals have, during crystallization, undergone such a heterovalent vacancy coupled (HVVC) substitution to a moderate extent. Then there are two conceivable cases in which the original structure types basically remain preserved as building modules for the structures of the resulting crystals.

The first case is such that the original structures are adaptable to house the available  $\text{Me}'^{3+}$  and vacancies in the structures. In this simple case, it is quite obvious that the original structure types are essentially conserved. From a number of such examples which we may find, we cite here an example which we have come across recently. It is a material having the chemical composition



This material happened to be obtained while we were trying to synthesize  $\text{CaGeO}_3$  in which  $\text{Y}^{3+}$  was doped. It was successful when the  $\text{Y}^{3+}/\text{Ca}^{2+}$  ratio of a starting material was close to the  $\text{Mn}^{2+}/\text{Ca}^{2+}$  ratio in  $\text{Ca}_5\text{Mn}[\text{Si}_3\text{O}_9]_2$  which is a representative chemical composition for the bustamite solid solution (Takéuchi *et al.*, 1976; Ohashi and Finger, 1978). The structure analysis of the colorless transparent crystals thus obtained confirmed the above chemical composition. The  $\text{Y}^{3+}$  ions in the structure are located at a specific site denoted as M3, which is characteristic of the bustamite structure type (Peacor and Buerger, 1962) and fully occupied by  $\text{Mn}^{2+}$  throughout the bustamite solid solution range (Fig. 1). The occupancy of  $\text{Y}^{3+}$  at the site has been found to be 0.8, leaving 0.2 vacancies at the site. If the  $\text{Y}^{3+}$  occupancy in the site were  $2/3$ , the local charge balance would have been perfectly attained. Since the  $\text{Y}^{3+}$  occupancy is slightly higher than that value, a minor amount of

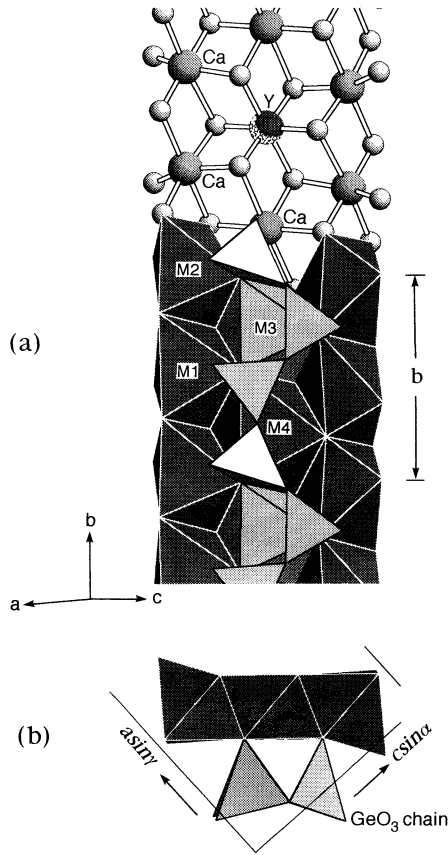


Fig. 1. (a) Showing the distribution of yttrium atoms in the octahedral band of  $\text{Ca}_{4.8}\text{Y}_{0.8}[\text{GeO}_3]_6$ . One of the  $\text{GeO}_3$  tetrahedral chains, flanked on it, is shown together. (b) Polyhedral diagram showing the end view of (a).

vacancies are distributed over another cation site M1 to attain crystal neutrality (See Appendix 3.2 for further details of the structure).

The second case will be such that the original structure (parent structure) is collapsed into layers (columns or blocks) and they get together to form a new structure. The original structure type thus remains preserved in those building modules of the resulting structure. In other words, the parent structure type is conserved as substructure of the resulting crystal structure.

The modules, layers (or slabs) for example, in those structures are in general related to each other by crystallographic operations, including those characteristic of space groupoids. They may hence be called structures based on cell-twinning. If such a 'cell-twinning' occurs not regularly but incoherently and locally in a crystal structure, the interface between a pair of slabs will be called a plane defect of the crystal.

One of the salient features of the structures in this second case is that they generally do not carry crystallographic vacancies in spite of the existence of Me' atoms substituting for Me atoms in the slabs to a certain extent. The process of formation of such crystals consisting of layer modules would presumably annihilate vacancies which would otherwise remain existed in the structure.

The series of structures which will be discussed in subsequent chapters belong to this second case. The substitution scheme of the chemical series which will appear in Chapter 6, in particular, is not exactly related to the relation (2). The cation involved in this specific substitution scheme is, however, such that it gives rise to a steric distortion in the parent structure owing to *d* electron orbitals characteristic of the ionic state. In any case, it will be seen that the variation in chemical composition from one structure to another in a structure series is expressible as a function of breadth of the layer modules (=units of cell-twinning).

Finally, note that the structure such as that of  $V_7O_{13}$ , a CS structure cited previously, corresponds to a special example of structures in the second case in which  $Me' = Me$  and cell-twin operations are simple slips. General discussions on those crystals characteristic of so called planar defects will be found in the illuminating review by Tilley (1980) and Hyde *et al.* (1979).

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