

## Effect of cation radii on the formation of complex oxide crystals

Valery I. Chani\*

Department of Materials Science & Engineering, McMaster University, 1280 Main Street West, Hamilton, Ontario, L8S 4L7, Canada

The effect of cation size on the structural stability of various oxide materials is discussed based on experimental observations of segregation, phase formation, congruency, and other parameters determining crystal growth conditions. The results indicate that the procedures necessary for optimization of crystal composition include growth of mixed crystals, composition analysis, calculation of segregation coefficients, and estimation of the relationship between the structural stability of the end member compounds forming the mixed crystals.

Key words: Oxide crystal, garnet, structural stability, cation size, segregation, mixed crystals.

### Introduction

As research and production of crystals continue to increase, a number of important materials are not available in single crystal form because of difficulties related with chemical and physical properties of the desired target materials and especially incongruent melting. Much effort, time, and resources are necessary to develop growth processes that result in high quality crystals of these compounds.

Because most of the known crystals melt incongruently, and because growth of such materials is possible only from the melts of compositions different from that of the desired compounds, many important crystals cannot be produced with a size and quality necessary for industrial applications. Existing research findings [1-6] indicate that the nature of incongruent melting particularly depends on the relation between structural stability (Fig. 1) of the desired target and the undesired foreign phases in the melts of stoichiometric composition of the target phase at the growth conditions (melting temperature). Thus knowledge about the stability of any oxide phase [1-3] might help to understand the ways and directions of improvements of existing materials.

This report discusses experimental procedures that allow the preliminary design and final growth of new complex oxide crystals: bulks, fibers, and films through the routine study of structural stability (Figs. 1-2) of selected structures and the modification of the original phase diagrams. The aim of the study is to determine equilibrium (most stable) compositions for all crystalline

phases that are formed in the melts corresponding to the vicinity of the stoichiometric composition of the target material. These data can be used to develop new original growth procedures and to improve existing ones.

### Experimental Procedures

The research scheme is based on the statement that oxide materials with the same structure have different structural stabilities [3, 4] depending on the kind and size of cations located in specific crystallographic sites

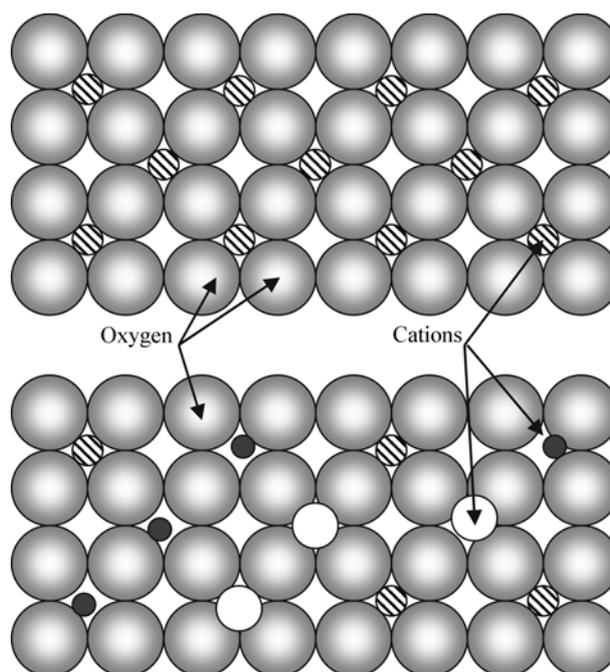


Fig. 1. Stable (above) and unstable (below) oxide structures.

\*Corresponding author:  
Tel : +1 905 525 9140 (ext.24485)  
Fax: +1 905 528-9295  
E-mail: chaniv@mcmaster.ca, vchani@yahoo.com

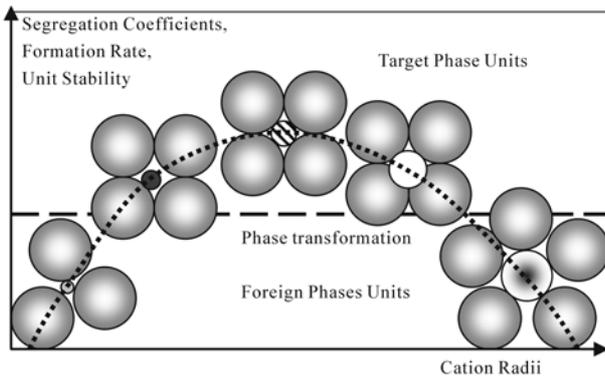


Fig. 2. Stability of cation site.

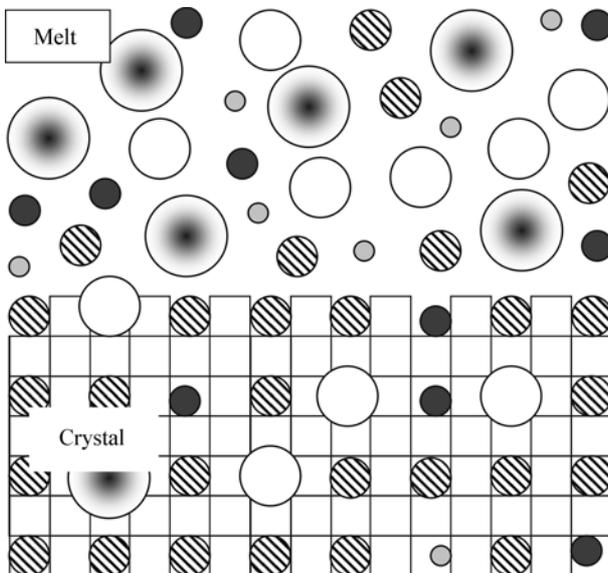


Fig. 3. Growth of mixed crystals.

as illustrated in Figs. 1 and 2. The relationship between the effects of cation charge and cation size on the bonding strength between the cation and the structure is unclear. Therefore only the effect of cation size on the formation of the oxide phases is discussed here to simplify the general understanding of the melt/crystal system.

Modification and optimization of crystal composition for selected structures can be performed based on the known tendencies [1-5]. The methods necessary for this optimization include (a) growth of mixed crystals (Fig. 3), (b) composition analysis, (c) calculation of segregation coefficients, and (d) estimation of the relationship between the structural stability of the end member compounds forming the mixed crystals. Melt and flux growth, liquid phase epitaxy (LPE), Czochralski (CZ), micro-pulling-down ( $\mu$ -PD) and other melt-related techniques are suitable for the mixed crystal growth.

### Segregation

Segregation of number (more than two) isovalent

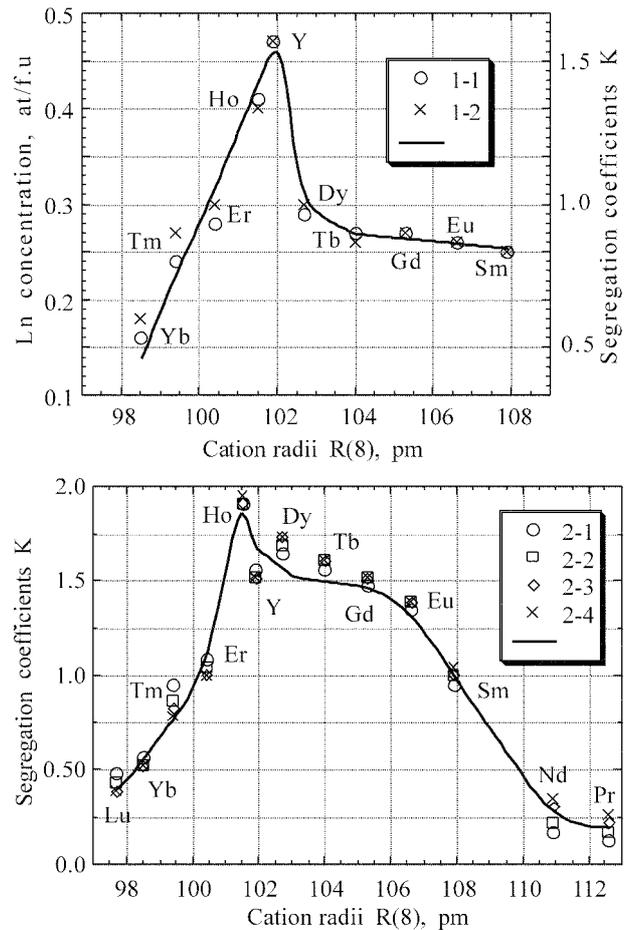


Fig. 4. Dependence of concentration (in atoms per garnet formula unit) and segregation coefficients of rare-earth cations  $\text{Ln}^{3+}$  in the  $(\text{ZLn})_3\text{Fe}_5\text{O}_{12}$  mixed garnet films (above) and segregation coefficients of  $\text{Ln}^{3+}$  in the  $(\text{ZLn})_3\text{Ga}_5\text{O}_{12}$  films (below).

cations can be studied in one crystal growth experiment also. Putting equal amounts of different cations together into the melt will result in equal conditions determining the rates of transportation and deposition of the particles from the melt onto the crystal surface. Therefore incorporation of the cations into the crystal will depend only on the strength of bonding between the cation and the structure (Fig. 4).

Generally almost any crystal growth technique based on solidification from the melt can be used for the fabrication of mixed crystals. Nevertheless some conditions should be applied when possible:

(a) The concentration of the end member compounds in the melt should be equal to ensure equal conditions for the desired phase formation of both end member compounds,

(b) The concentration of the end member compounds should be as low as possible to decrease the effect of the interaction between the end members in the melt and the possible formation of clusters or intermediate phases that by chance will effect the segregation between the melt and the mixed crystal

(c) The growth rate should be as low as possible to

ensure equilibrium conditions at the vicinity of the melt/crystal interface. On the other hand application of a low growth rate will increase accuracy of the segregation measurements as follows from the Barton, Prim and Slichter (BPS) equation [7]. Thus, a flux growth technique is preferable to melt growth ones: Czochralski, micro-pulling-down ( $\mu$ -PD) fiber growth [1, 2, 5, 6], and others. Surprisingly in spite of a very high growth rate ( $1\text{--}10\text{ mm minute}^{-1}$ ), segregation in the  $\mu$ -PD process is also detectable. Sometimes this technique allows fabrication of single crystals of incongruently melting materials from the melts that contain small (5-10 mol.%) amounts of flux. As an example, incongruently melted  $\text{KNbO}_3$  crystals were grown using  $\text{K}_2\text{O}$  flux [8]. Therefore this method is also appropriate for a determination of the relationship between segregation coefficients through growth of mixed crystals.

### Stability Diagram

The dependence of the segregation coefficients on cation radii can be interpreted as stability diagram. A high segregation coefficient can be considered as measure of bonding strength between the cation and the crystallographic site in the oxide matrix. The problems related with growth of high quality oxide crystals are generally very similar. The stability of a foreign (undesirable) phase is often greater than that of the target (desirable) phase at the established growth conditions. Therefore the formation of the foreign phase is sometimes preferable, and therefore the target material melts incongruently. This way growth of the desired crystals from the melt of the same composition is difficult or impossible.

However, the original phase diagram can be modified by a corresponding correction of the composition of both the target and foreign materials [1-3]. For example, as the stability of the target phase increases nucleation and growth of the foreign phase becomes difficult or impossible. Microscopically cation size and the strength of chemical bonding between the cation and the structure (Figs. 2-3) determine [3] the kinetics of incorporation of any particular cation into the structure. This is why growth of mixed crystals is considered an appropriate method for study of structural stability.

### Growth of Mixed Crystals

The stability of garnet ( $\text{Y}_3\text{Al}_5\text{O}_{12}$ ), langasite ( $\text{La}_3\text{Ga}_5\text{SiO}_{14}$ ), huntite-borate ( $\text{YAl}_3(\text{BO}_3)_4$ ),  $\text{KTiO}(\text{PO})_4$  (KTP), and other structures, that have several types of cation sites have been particularly studied and discussed in [1-3].  $\text{Tb}_3\text{Al}_5\text{O}_{12}$  (TAG) garnet is good example of the practical application of this approach [1, 2]. Growth of TAG crystals by conventional melt growth techniques (Czochralski method) from the melt of  $\text{Tb}_3\text{Al}_5\text{O}_{12}$  composition is almost impossible because of incongruent melting [9]. The  $\text{TbAlO}_3$  (TAP) perovskite phase primarily crystallizes

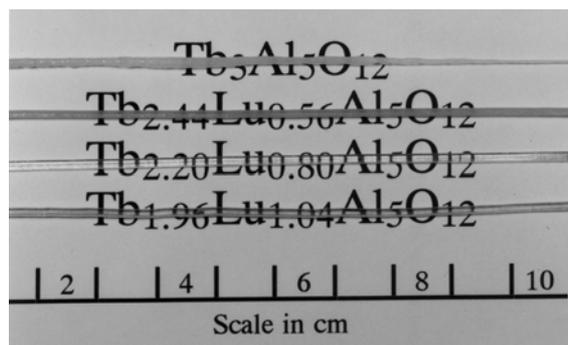


Fig. 5. View of  $(\text{Tb,Lu})_3\text{Al}_5\text{O}_{12}$  fiber crystals.

in a stoichiometric  $\text{Tb}_3\text{Al}_5\text{O}_{12}$  melt instead of the garnet phase. The information about structural stability of both target (TAG) and foreign (TAP) phases was successfully applied for modification of incongruently melting  $\text{Tb}_3\text{Al}_5\text{O}_{12}$  by partial substitution of  $\text{Tb}^{3+}$  with  $\text{Lu}^{3+}$  and other small rare-earth cations.

The substitution phenomenon in the  $(\text{Tb,Lu})_3\text{Al}_5\text{O}_{12}$  and  $(\text{Tb,Yb})_3\text{Al}_5\text{O}_{12}$  mixed crystals have been studied by solidification of corresponding melts using a micro-pulling-down method. The  $\mu$ -PD apparatus, based on RF heating of the crucible, was used for the growth of the fiber crystals with a relatively high melting point ( $2000^\circ\text{C}$ ).

It was found that with substitution of  $\text{Tb}^{3+}$  with  $\text{Lu}^{3+}$ ,  $\text{Yb}^{3+}$ , and/or  $\text{Tm}^{3+}$ , the tendency of  $\text{TbAlO}_3$  perovskite phase formation in the  $\text{Tb}_3\text{Al}_5\text{O}_{12}$  melt decreases. Then growth of  $(\text{Tb,Lu})_3\text{Al}_5\text{O}_{12}$  and other related mixed crystals from the melt of the same composition becomes possible (Fig. 5). In the case of  $(\text{Tb,Lu})_3\text{Al}_5\text{O}_{12}$  crystals, an invariant point was found to exist in the vicinity of the  $\text{Tb}_{2.2}\text{Lu}_{0.8}\text{Al}_5\text{O}_{12}$  composition. Therefore uniform (chemical composition, phase, lattice parameter) single crystal fibers of the above material up to 500 mm in length and about 1.3 mm in diameter were produced at pulling-down rate of  $1.2\text{ mm minute}^{-1}$ . In a similar manner, a correction of composition for other oxide crystals is expected.

Generally growth of mixed crystals is quite difficult or impossible, because segregation between the end member compounds results in a non-uniform distribution

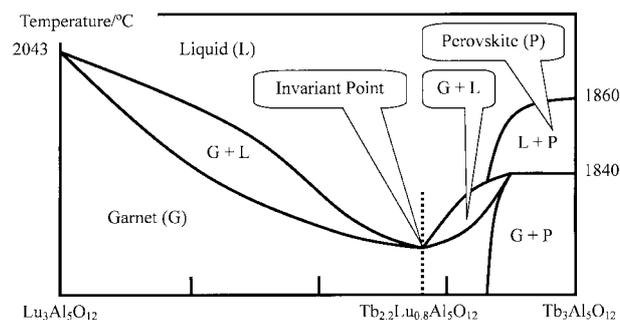


Fig. 6. Phase diagram for the  $\text{Lu}_3\text{Al}_5\text{O}_{12}$ - $\text{Tb}_3\text{Al}_5\text{O}_{12}$  system proposed.

of constituents along the growth axis, a variation of lattice parameters, and mechanical stresses. This is a common understanding of the behavior of mixed oxide systems [10]. Growth of high quality  $(\text{Tb,Lu})_3\text{Al}_5\text{O}_{12}$ ,  $(\text{Tb,Yb})_3\text{Al}_5\text{O}_{12}$ , and  $(\text{Tb,Tm})_3\text{Al}_5\text{O}_{12}$  mixed garnet crystals from the melt and other experimental results show that these systems are most probably described by a diagram type given in Fig. 6. This diagram is considered as a combination of the diagram with unlimited miscibility and minimum melting point and a conventional diagram with a peritectic reaction.

### Summary

The experimental procedure that allows an understanding of the relationship between bonding strength of various cations in oxide structures was discussed. In the main, crystal growth of mixed crystals and composition measurement facilities are the main techniques necessary to process this research scheme.

It is important to prove the applicability of the described practice for other important oxide materials (laser, magneto-optical, and non-linear optical crystals, etc.), as well as to develop advanced techniques for the study of structural stability and growth of mixed crystals for optoelectronic and other technical applications.

According to other observations [3, 4], the maximal

field of phase formation on a phase diagram and a high probability of congruent melting characterize the crystals formed by equilibrium cations (Fig. 2) and have maximal structural stability. Most probably these crystals have minimal solubility in solvents and good mechanical properties due to strong bonding between crystal particles.

### References

1. V.I. Chani, A. Yoshikawa, H. Machida, and T. Fukuda, *J. Cryst. Growth* 212[3-4] (2000) 469-475.
2. V.I. Chani, A. Yoshikawa, H. Machida, and T. Fukuda, *Mater. Sci. & Eng. B* 75[1] (2000) 53-60.
3. V.I. Chani, K. Shimamura, Y.M. Yu, and T. Fukuda, *Mater. Sci. & Eng. R20* (1997) 281-338.
4. V.I. Chani, in "Proc. SPIE", *Thin Films in Optics*, 1125 (1989) 107-114.
5. V.I. Chani, A. Yoshikawa, Y. Kuwano, K. Hasegawa, and T. Fukuda, *J. Cryst. Growth* 204 (1999) 155-162.
6. V.I. Chani, A. Yoshikawa, H. Machida, T. Satoh, and T. Fukuda, *J. Cryst. Growth* 210 (2000) 663-669.
7. J.A. Burton, R.C. Prim, and W.P. Slichter, *J. Chem. Phys.* 21 (1953) 1987-1991.
8. V.I. Chani, K. Shimamura, and T. Fukuda, *Cryst. Res. Technol.* 34 (1999) 519-525.
9. S. Ganschow, D. Klimm, P. Reiche, and R. Uecker, *Cryst. Res. Technol.* 34 (1999) 615-619.
10. D. Mateika, E. Völkel, and J. Hisma, *J. Cryst. Growth* 102 (1990) 994-1013.