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Experimental evidence that a high electric field acts as an efficient external parameter during crystalline growth of bulk oxide

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ABSTRACT

A new crystal growth device, in which a high static external electric voltage (up to 14 kV) is added to a floating zone method, is described. Our first experiments show that the application of such an electric field acts like an external force, introducing a pressure effect which is in direct competition with temperature in the solid/liquid thermodynamic equilibrium. High electric fields could therefore be an additional parameter in crystal growth, opening original routes to the synthesis of new materials.

1. Introduction

Availability of high quality single crystals is essential for the study of intrinsic anisotropic physical properties of compounds. Crystal growth is conditioned by many parameters that involve complex thermodynamic and kinetic laws. The key to success, in crystal growth, consists in reaching an optimal thermodynamic equilibrium between the liquid phase (molten zone) and the solid phase (seed crystal). Among the various crystal growth techniques, the optical floating zone method was clearly shown in recent years to be a powerful one in a wide range of applications and for the study of both single crystal growth parameters and phase diagrams. The principle of this technique avoids using any crucible, therefore preventing possible chemical reaction between melt and crucible material. This method also allows the use of a traveling solvent procedure necessary to grow incongruently melting materials and also solid solutions with uniform compositions [1]. Besides, the technique allows also to modulate the thermal gradient at the solid–liquid interface by modifying the geometry and the nature of the heating lamps used, the growth speed and the system chemistry (composition of the feed rod, composition of the solvent, when used, and gas flow); it is also possible in such a technique to modulate the partial pressure of the gas surrounding the molten zone. Previous studies have reported that this last parameter is able to convert incongruent-melting into congruent-melting [1,2]. The Gibbs free energy of the system can be consequently written with an additional term PV, in the form:

$$G = U - TS + PV. \quad (1)$$

In other words, a congruent-melting state is observed if the chemical potential of the liquid phase becomes equal to the solid one; thus, application of gas pressure moves boundaries in solid–liquid phase diagrams by competing with thermal energy [3].

Interestingly, an electric field can also act on thermodynamic laws and on the solid/liquid interface during a growth process. Earlier studies have also shown that it is possible to modulate the morphology [4,5] and the microstructure [6,7] of a crystal by applying an electric current or an external electric field during growth. They both can affect the nucleation process [8–11], but also the partitioning of ions inside the molten zone during growth [4,12,13]. On one hand, crystallization under an electric current has been widely investigated but mostly on conductive materials showing that besides the change in chemical potentials induced by the electric current, several other phenomena occur during the growth process [10]. Butler and Volmer [14] showed that charge transfer phenomenon inducing nucleation can be ruled by the overvoltage. Moreover, it has been shown that the flow of an electric current can substantially alter the supercooling of the melt

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by Peltier thermoelectric cooling [15] or, at the contrary, by Joule heating [15–17], therefore modifying the driving force of the crystal growth. Finally, Lorenz force [16,17] caused by an electric current pulse or electromigration [15] induced by a current flow both promote mass transport which can affect the crystal growth's rate and its quality. On the other hand, growth under an external electric potential leads to the addition of a free energy term to the Gibbs free energy [9] whose influence is bound to the dielectric permittivity of the involved medium:

$$G = U - TS + PV + \S\varepsilon E^2 V \quad (2)$$

where ε is the dielectric permittivity, E the electric field strength and V the volume.

Several studies, done at the microliter or milliliter level (by monitoring growth under a microscope), have shown that an external electric field can noticeably modify the phase diagram of a material by disturbing the equilibrium between the chemical potentials of solid and liquid phases [18–20]. In a system made of a high-temperature conductive oxide melt, Uda et al. have shown that most of the applied external electric potential is consumed in the electric double layer (EDL) which is presumably generated at the interface between the melt surface and the atmosphere, or at the boundary between melt and crystal embryos [20]. A huge electric field is expected to form at these boundaries: the authors have demonstrated that an electric field as high as 10^4–10^5 V/cm can be generated at the EDL during crystal growth of langasite ($La_3Ga_5SiO_{14}$) when applying an external electric field of 600 V/cm [20]. As an example, such a high field could convert an incongruent-melting state into a congruent-melting one. Indeed, by developing the chemical potential expression η_L^j (for the species j in the L phase), they deduced the general expression:

$$\eta_L^j = \eta_{0_L}^{\ j} + kT\ln\left(\gamma_L^j C_L^j\right) + z_L^j eV + \frac{\partial}{\partial C_L^j}\left[\frac{1}{2}\left(\varepsilon_L E^2 + m_L H^2 + \frac{1}{c_L}\sigma^2 + \ldots\right)\right] \quad (3)$$

where, for the jth species in the liquid phase, γ_L^j is the activity coefficient, C_L^j its concentration, z_L^j the valence of the ion, e the elementary charge, V the local potential and ε_L, m_L and c_L are respectively the dielectric permittivity, the magnetic permeability and the elastic compliance of the liquid phase.

A similar expression can be derived for the solid state by changing L for S. Eqs. (2) and (3) highlight the fact that a gas pressure (P, σ), an electric field (E, V) but also a magnetic field H, compete with temperature T in the equilibrium occurring during crystal growth. Since dielectric permittivity ε_i, magnetic permeability m_i and elastic compliance c_i ($i=S$ or L) are different in the liquid and solid phases, we understand how, during crystal growth, external parameters such as E, H and σ can act on the chemical potentials η_S and η_L; consequently shifting equilibrium between phases towards higher or lower temperatures, altering the fractions of solid and liquid in the liquid phase, and finally converting incongruent into congruent melting behavior of the material.

In this paper we report the development of a prototype device for floating-zone growth under an intense static electric field. The device enables realization of a high electrical tension, up to the breakdown voltage, between two electrodes spaced by 2.5 cm. To our knowledge, this is the first time that a crystal growth device involving an external electric field has been associated with a mirror furnace. Besides, this set-up allows, for the first time, to study the impact of high electric field on a centimeter-size liquid–solid interface, and test previous predictions (see Eq. (3)), and micro-scale observation [18]. This development is an additional example of the great progress made since the development of the first vertical floating zone furnace in the early fifties [21].

2. Experimental details

We tested our new device on the growth of crystals of $BaCo_2V_2O_8$, a compound displaying a relatively low and congruent melting temperature (1020 °C). Lejay et al. have already reported growth of such a compound in an ordinary image furnace [22].

$BaCo_2V_2O_8$ was prepared by solid-state reaction: reagent powders of $BaCO_3$, Co_3O_4 and V_2O_5 were weighed and mixed in stoichiometric proportions. The mixed and ground powders were pressed (2500 bars) and placed in an alumina boat and heated at 900 °C for 72 h. Phase purity was checked by X-ray diffraction. The obtained samples were then crushed and shaped into cylindrical rods of 5 mm diameter. The rods were sintered at 900 °C during 24 h. Crystal growth was conducted under air at a growth rate of 3 mm/h with a counter-rotation rate of 20 rpm. Electric field was applied through a high voltage generator (Spellman SL10, 10 mW).

The external electric field device used was developed to be compatible with the geometry of an NEC SC-N15 HD optical furnace (Fig. 1a) equipped with two lamps of 1500 W nominal power each, a sealed quartz enclosure allowing gas pressure up to 10 bars and a camera monitoring to follow progress of the growth. It is based on a lower alumina support and two pierced alumina shafts attached to the support with cement. The metallic wires used to carry the voltage are placed along the inside of the alumina shafts to protect them from the heat and to avoid any

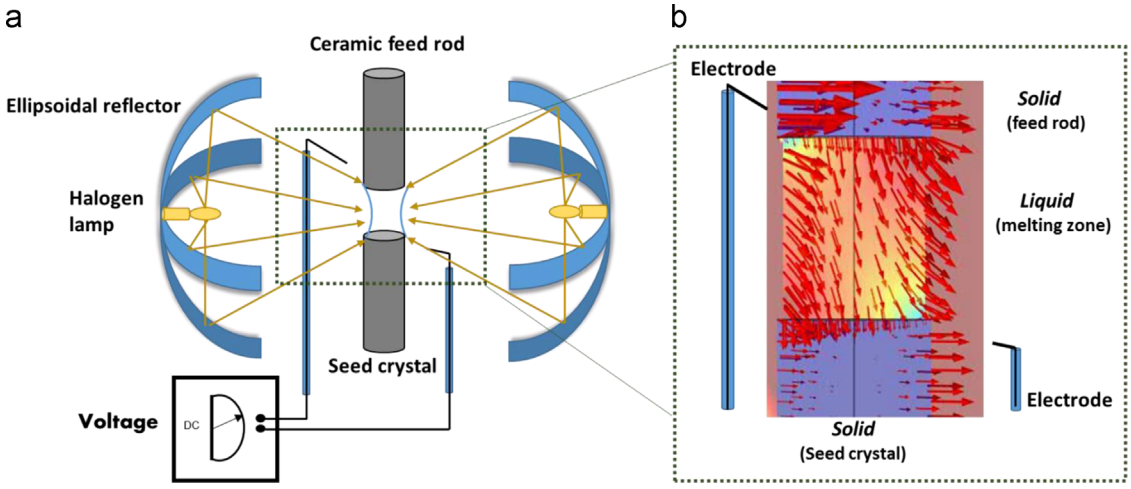

Fig. 1. (a) Experimental set-up (2 mirrors optical furnace equipped with a high electric field supply). (b) Simulation of electric field at melted zone interfaces (arb. units).