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Axial vibration control of melt structure of sodium nitrate in crystal growth process

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ABSTRACT

The melt structure evolution under the action of the low-frequency axial vibration control (AVC) technique was studied *in situ* by Raman spectroscopy for several complex chemical compound melts: sodium nitrate, margarine acid, paraffin mixture (C_{17}-C_{20}). The measurements were conducted in the temperature range from the melting point up to 60 °C above. Comparison of crystallization heats for AVC activated and steady melts with melting heats of AVC-CZ and conventional CZ produced powders allowed to propose the energy diagram of $NaNO_3$ states for activated and non-activated melts and crystals based on DTA, XRD, DSC and Raman experimental data.

1. Introduction

The problem of the effective heat-mass transfer in melt-crystal growth technologies plays a significant role in production of high quality crystals. The fluid flow can modify the effective segregation at the interface, producing macro-segregation with adverse effect (striations in crystals, increase of dopant level during growth). To control heat-mass transfer in melt-crystal growth a number of techniques was successfully applied for the past 20 years (see review [1] and references therein). Among these techniques the low-frequency axial vibration control (AVC) technique demonstrated enviable perspectives for its universe application to efficient heat mass transfer in Bridgman, CZ, VGF and other melt-growth techniques as well as crystal quality enhancement [2].

Structural changes and alteration of properties in material during the melting process and after that are supporting the idea of heritage between solid and liquid phase [3]. It may be said that the melt at a temperature range closed to the melting point has a structure more similar to the solid phase, then to the gas phase [4]. The more distinctly this situation is observed in case of thermotropic liquid crystal materials [5]. Nowadays, the melt structure of pure metals and metal alloys are more studied in detail [6]. For complex inorganic compounds one of the most studied melts are borates investigated by high temperature Raman spectroscopy [7]. In case of complex semiconductors ($A^{III}B^{V}$, $A^{II}B^{VI}$) the structural changes vary significantly but to the moment there are no reliable data on structures of complex semiconductors melts and pathways to control them.

In the present research we tried to prove the hypothesis about the AVC technique as an efficient instrument for structure control of melts of complex chemical compounds of different nature.

2. Experiment techniques

2.1. Raman spectra experiments

To prove the hypothesis about AVC-melt dissociation we analyzed sodium nitrate melt by Raman spectroscopy.

2.1.1. Raman cell

A setup for Raman spectrum measurements of melt activated by AVC was designed (Fig. 1). We made an isothermal aluminum cell, in which the AVC was induced in melt by a quartz glass disk oscillation.

The specific feature of the setup is 0.2 mm quartz glass window for Raman measurements in geometry of photon backscattering. Raman spectra were obtained using Ocean Optics QE6500 spectrometer supported by 785 nm excitation laser and optical fiber cable for input/output of light signal. Integration time was 30 s for the every run in the range 200–2000 cm^{-1}. It was enough to collect Raman photons at 500–1000 mW laser pumping power and to avoid the Raman probe overheating. The laser beam was focused in 7.5 mm distance from the probe output window and the focus point was in the melt in the middle between the quartz window and the oscillating disk (Fig. 2 point #1). The laser beam passed

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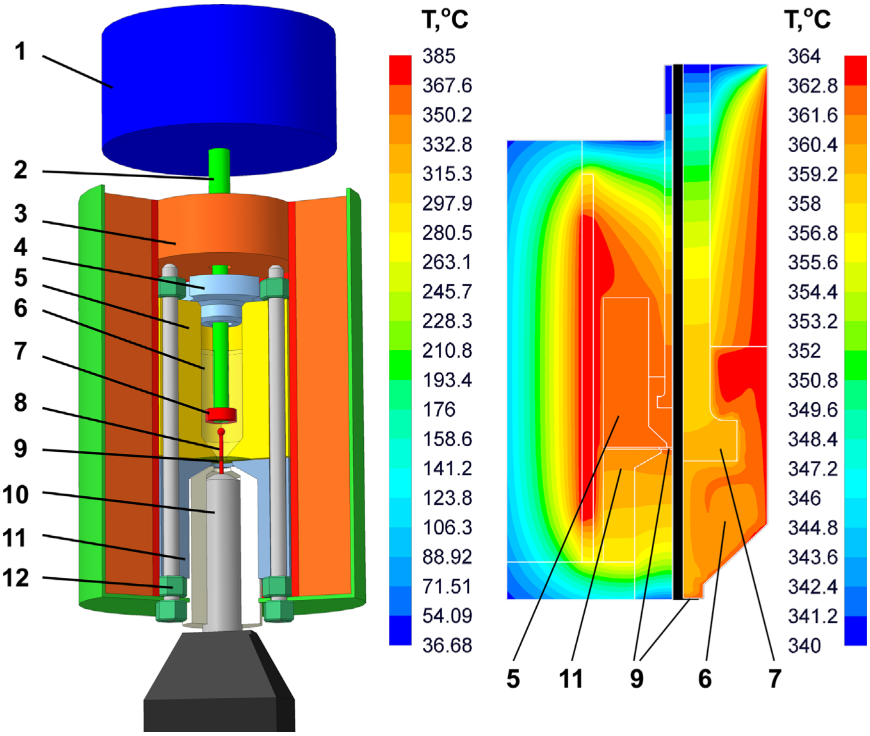

Fig. 1. Scheme of setup for Raman measurements of the melt, activated by AVC (left) and temperature distribution into the cell (right). 1-vibrational mechanism, 2-rod, 3-kaolin wool thermoinsulating cover, 4-aluminium cover, 5-cell body, 6-melt, 7- oscillating baffle, 8- laser beam, 9-quartz glass window, 10- Raman probe, 11- body face, 12-screw.

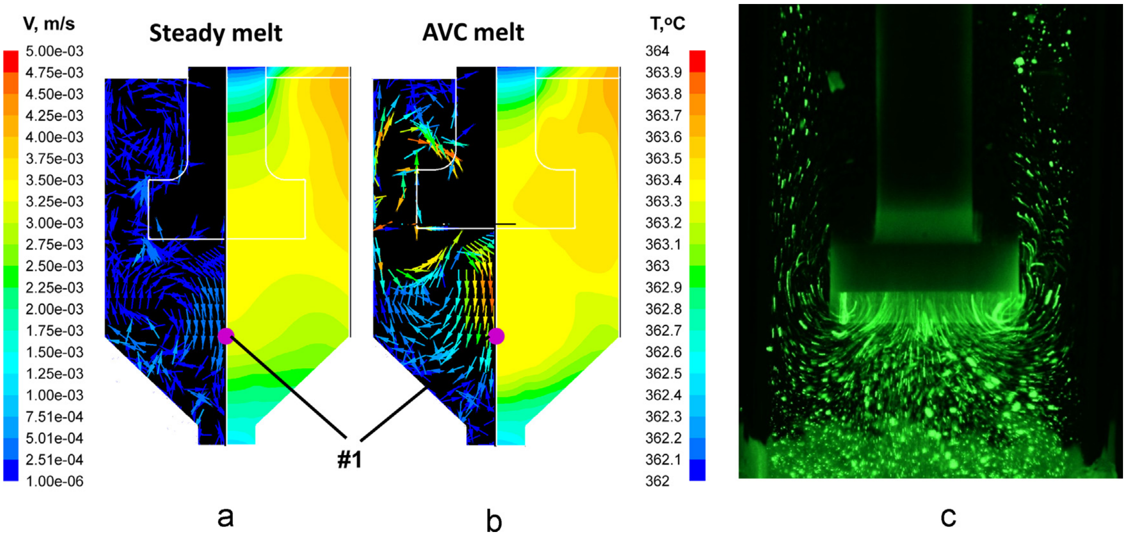

Fig. 2. Distributions of velocity vectors (left-hand side) and temperature (right-hand side) for steady (*a*), AVC activated (***A***=0.7 mm and ***f***=25 Hz) $NaNO_3$ melt (*b*) and experimental flow's picture (*c*). The point #1 shows the position of the laser focus of the Raman probe.

through 4 mm melt/solid layer. The spot diameter was 0.3 mm. Thus the power density of laser emission in the point was as high as 110 kW/cm^2.

We checked the influence of quartz glass on a Raman spectrum by measurements the spectra through the glass and from the free surface and found out that in the temperature range 25 °C to 324 °C for solid/liquid $NaNO_3$ (see Suppl.), margarine acid and paraffin mixture the spectra were identical.

2.1.2. Numerical simulation

Experimental cell for Raman-spectrum measurements (Fig. 1) has been numerically analyzed with ANSYS 14.5 Fluent software. 2D geometry for two cases, one including the cell and the furnace and the other inner volume of the cell with the melt, gas and vibrating baffle, has been covered with tetrahedral cells of 0.2 mm general size. To obtain the solution for the temperature distribution and flow field in the melt the Pressure Based solver (Boussinesq approximation) with PISO pressure-velocity coupling scheme has been used in the case of enable vibrations and for thermal conductivity in solid zones - standard FLUENT equations set [8]. As initial boundary conditions constant temperature on the heating zone and convective heat transfer with ambient temperature 25 °C on outer walls has been applied. Physical properties for all applied materials are summarized in Table 1.

To visualize the flow's patterns in case of margarine acid and paraffin mixture we used a transparent cell made from quartz glass similar to that was described in Ref. [9]. According to