MS17-P8 Garnet inclusions in diamond: The role of elastic properties

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Although inclusion-bearing diamonds are so rare (about 1% of the diamond retrieved), they are geologically relevant because they are the only direct and unaltered samples that we have from the Earth's mantle. Investigation of mineral inclusions still trapped in diamond allows retrieving several pieces of information about the Earth's interior and its active geodynamics (e.g. providing the definition of the initiation of subduction processes, capturing the redox state of the mantle etc… [1]).Therefore it is clear that the determination of the entrapment pressure (i.e. depth of formation) of these mineral inclusions is a fundamental tile for the understanding of the Earth's mantle dynamic as it allows constraining the chemico-physical environment in which diamond and their inclusions formed. The recently developed 'elastic geobarometer' method [2] allows retieving the entrapment pressure for a diamond-inclusion pair provided the knowledge of the thermoelastic parameters for both diamond and inclusion.Since mineral inclusions in diamonds from the subcratonic lithospheric mantle are mostly represented by garnet (38%) together with olivine (18%), clinopyroxene (16%), orthopyroxene (8%), Mg-chromite (18%) and sulphides (2%) our study has been focused on the determination of reliable elastic properties for endmember garnets (e.g. pyrope, almandine, grossular and uvarovite). Knowledge of the thermoelastic properties for endmember garnets should in principle allow calculating thermoelastic parameters for potentially any garnet composition commonly found in diamond. In particular, here we present the investigation of endmember garnets thermal expansion by in situ single crystal X-ray diffraction at high-temperature conditions. The measurements have been performed on the same crystals used by [3] for their high-P investigation adopting the same methods for the unit-cell parameters determination (e.g. 8-position centring using SINGLE software, [e.g. 4, 5]). Further details on the high temperature apparatus and measurements method here adopted are reported in [6]. The thermal expansion so calculated allowed retrieving the entrapment pressure 5.67 GPa at 1500K for an eclogitic garnet with composition Py51Al22Gr27.

References [1] Shirey et al. (2013) RiMG, 75, 355. [2] Angel et al. (2014) Am Mineral, 99, 2146. [3] Milani et al. (2015) Lithos, in press [4] King and Finger (1979) JAC, 12, 374. [5] Angel and Finger (2011) JAC, 44, 247. [6] Alvaro et al (2015) JAC, submit.

Keywords: Diamond, Inclusion, Diffraction, Mantle, Garnet

MS17-P9 Quantitative in situ study of salbutamol crystallization as a function of relative humidity and temperature

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Salbutamol, a β_2-adrenoreceptor agonist, is a common drug used for the treatment of bronchial asthma via inhalation. Spray dried salbutamol sulphate and salbutamol base particles intended for the use as active pharmaceutical ingredient in dry powder inhalers are amorphous as a result of spray drying (Littringer et al., 2013). However, the crystallization of the amorphous salbutamol particles may be triggered by exposure to humid air or by heating of the sample (Columbano et al., 2002). Knowing the critical conditions of salbutamol crystallization is essential for the correct handling and storage of the drug. In order to quantitatively characterize the process of salbutamol crystallization we performed a series of time- resolved powder X-ray diffraction experiments at variable temperature (25 and 35 °C) and relative humidity (60 %, 70 %, 80 %, 90 %). Quantification of amorphous-to-crystalline ratio as a function of time at variable temperature and relative humidity was performed using the Partial Least Squares Regression, PLSR (Degen et al.,2014; Zellnitz et al., submitted). We show that the crystallization speed of salbutamol sulphate and salbutamol base is a non-linear function of both temperature and relative humidity (Figure 1).

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Degen, T., Sadki, M., Bron, E., König, U., and Nénert, G. (**2014**) "The HighScore Suite," Powder Diff., **29(S2)**, S13-S18

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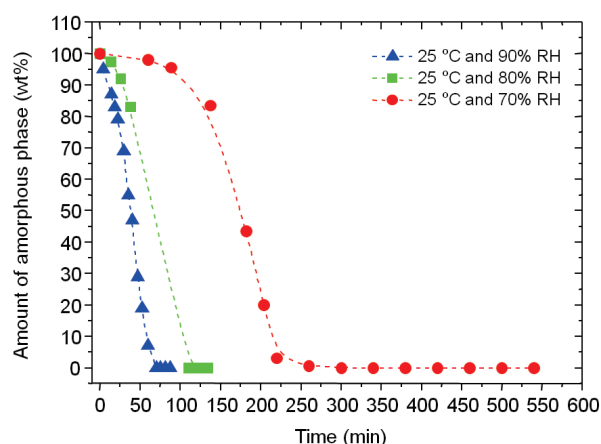
Figure 1. Amorphous-to-crystalline ratio for spray dried salbutamol plotted as a function of time at relative humidity of 70 %, 80 % and 90 %.

Keywords: Pharmaceutics, crystallization process, X-ray diffraction, partial least square regression

MS17-P10 In situ XRD study of reduction of $Mn_xZr_{1-x}O_2$ solid solutions

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Solid solutions based on ZrO_2 exhibit high catalytic activity in a number of practically important reactions. Mn-Zn mixed oxides can effectively catalyze the gas-phase oxidation of hydrocarbons or chlorcarbons. Mn cations can enter the lattice of ZrO_2 with the formation of solid solutions $Mn_xZr_{1-x}O_2$, in which lattice oxygen possesses sufficiently high mobility and hence high reactivity.

A series of mixed Mn-Zr oxides with different molar ratios Mn/Zr (0.1-9) have been prepared by coprecipitation of manganese and zirconium nitrates and characterized by XRD and N_2 adsorption techniques. It has been found that at low Mn/Zr ratios, when the Mn content is below 30 atom %, the catalysts are single-phase solid solutions ($Mn_xZr_{1-x}O_{2-\delta}$) based on a ZrO_2 structure. According to XPS data, manganese in these solutions exists mainly in the Mn^{4+} state. An increase in the Mn content mostly leads to an increase in the number of Mn cations in the structure of the solid solutions, but a part of manganese form Mn_2O_3 and Mn_3O_4 in crystalline and amorphous states.

Reduction of solid solutions in hydrogen was studied by a TPR, in situ XPS and XRD, at temperature range 100 to 700 °C. Figure 1 shows a series of diffraction patterns recorded during the reduction of the sample with Mn/Zr=1. At room temperature, the sample contains two phases: a solid solution $Mn_xZr_{1-x}O_4$ and Mn_2O_3. The reduction of this sample leads to a change in the lattice parameter of the solid solution $Mn_xZr_{1-x}O_4$, which is indicated by the shift of corresponding peaks to larger angles. Besides, the reduction leads to transformations of manganese oxides. The reduction of the solid solutions proceeds in a wide temperature range 100-700 °C via two steps. In the first stage, at temperatures of 100-500°C, manganese cations undergo partial reduction to Mn^{2+}, whose presence is confirmed by XPS measurements. The lattice parameter of $Mn_xZr_{1-x}O_2$ in this case varies because of changes in the oxidation state of manganese cations in the bulk of solid solution. In the second stage, at temperatures of 500-700°C, manganese cations exit from the bulk of the solid solution and segregate on its surface. The lattice parameter at this stage increases because of the decrease in the number of Mn cations in the oxide.