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Comments on "Thermoelectric properties of rare earth containing type-I clathrate compound, $Dy_8Al_{16}Si_{30}$"

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Abstract In the paper by K. Rajput and S. Vitta published in the present journal the synthesis and the thermoelectric properties of the dysprosium containing clathrate $Dy_8Al_{16}Si_{30}$ were reported. We prepared two samples following exactly to the technique described in the paper. Our XRD and SEM/EDX investigations do not confirm the presence of any amount of a Dy-containing clathrate phase in the sample.

In the recent paper by K. Rajput and S. Vitta [1] the synthesis and the thermoelectric properties of the dysprosium containing clathrate $Dy_8Al_{16}Si_{30}$ were reported. The authors obtained by melting the elementary metals a polyphase material containing, as claimed by the authors, the clathrate phase. This conclusion was made on the basis of X-ray powder diffraction (XRD) of the polyphase sample. However, in our opinion, the diffraction pattern and the Rietveld analysis given in the paper do not provide strong evidence of the presence of the clathrate phase. The authors investigated the sample also using the scanning electron microscopy (SEM) with energy dispersive X-ray spectral analysis (SEM/EDX). However, only the total composition of the sample and not that of the individual phases was reported.

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We prepared a sample following exactly to the technique described in the paper (Tetra-Arc Techno Search) with annealing of a part of the sample at 780 K for 7 days. The as-cast and the annealed samples were characterized by XRD (PANalytical XPert Pro MPD, X-ray Center TUWien) and SEM/EDX (Philips XL30 ESEM, EDAX New XL-30 135-10 UTW). The powder diffraction patterns obtained by us were very similar to the reported in Ref. [1]. The Rietveld refinement of the samples ($R_{wpr} = 2.8$ %) yields the following phases (mass. %): as-cast sample—Si 45, $DySi_2$ 22, $DyAl_2Si_2$ 17, Al 16; annealed sample—Si 59, $DyAl_2Si_2$ 28, $DySi_{1.78}$ 4; Al 7, $Dy_2Al_3Si_2$ 2 (Fig. 1).

No clathrate phase was detected in both our samples. Although the diffraction pattern of the Dy-clathrate is not available, it can be simulated based on the existing Ba- and Sr-containing analogues. Substitution of Ba with its ionic radius (r_{ion}) of 1.47 Å by Sr with $r_{ion} = 1.31$ Å results in a contraction of the unit cell from $a = 10.632$ to 10.465 Å [2, 3]. Linear extrapolation to the ionic radius of Dy^{3+} $r_{ion} = 1.083$ Å leads to a value of $a = 10.23$ Å for the lattice constant of the Dy-clathrate. Using this value and replacing the scattering factor of Ba by that of Dy we obtained the diffraction pattern of a hypothetical Dy-clathrate which is shown in Fig. 1 as a line diagram.

The polished surfaces of the samples were analyzed by SEM with EDX measurements of the compositions of all individual constituting phases (Fig. 2). The analysis confirms the presence of phases found by the powder diffraction.

No phase with the generic composition A_8B_{46} characteristic of a type-I clathrate was found.

Thus both XRD and SEM/EDX do not confirm the presence of any amount of a Dy-containing clathrate phase in the sample prepared according to [1].

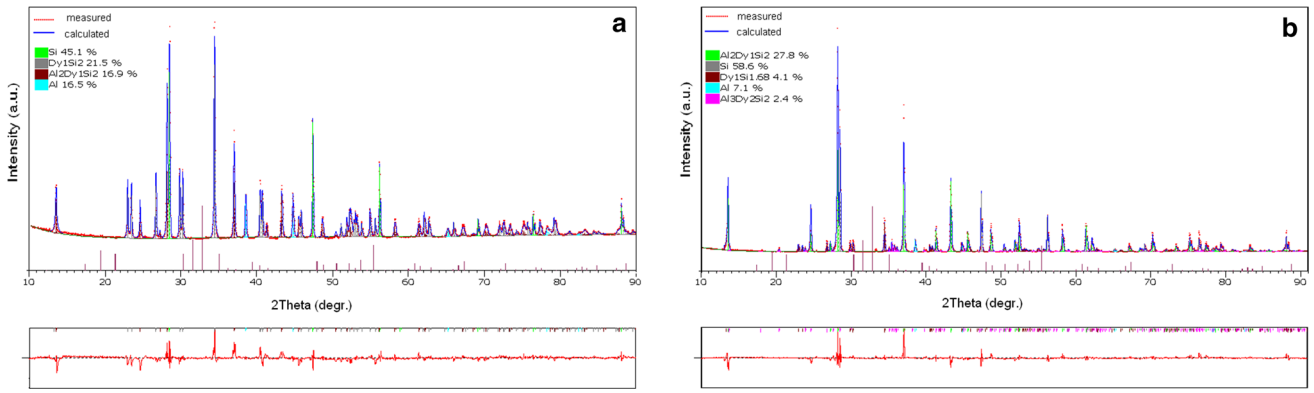

Fig. 1 X-ray diffraction patterns of the as-cast (**a**) and the annealed (**b**) samples with their Rietveld refinement profiles. The phase compositions are shown in mass. %. The *lines* show the positions and the relative intensities of the peaks of the hypothetical $Dy_8Al_{16}Si_{30}$ clathrate phase

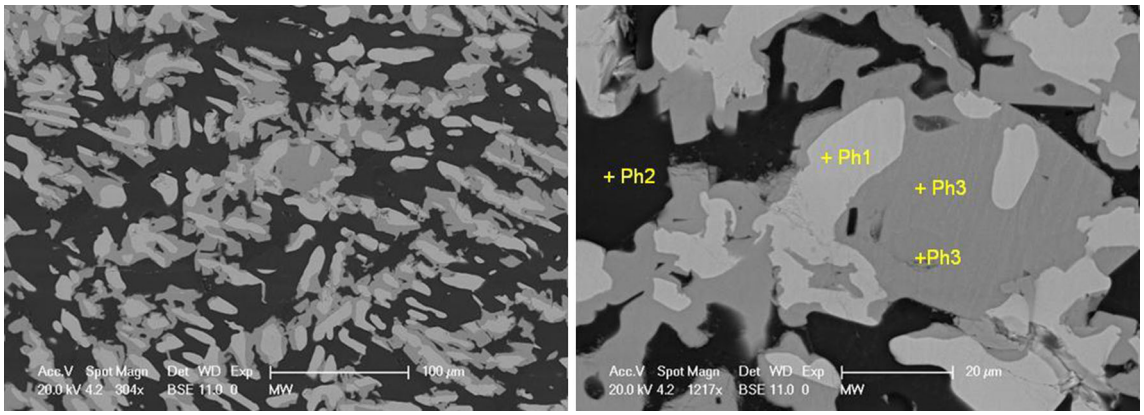

Fig. 2 SEM image of the polished surface of the as-cast sample at two different magnifications. The composition of the main phases: Ph1–$Dy(Si_{1-x}Al_x)_{1.75}$ ($x \approx 0.1$), Ph2–Si, Ph3–$DySi_{2-y}Al_{2+y}$ ($y \approx 0.1$)

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