

Hysteresis in the melting kinetics of Bi nanoparticles

E. Haro-Poniatowski^{a,d,*}, R. Serna^a, C.N. Afonso^a, M. Jouanne^b, J.F. Morhange^b, P. Bosch^c, V.H. Lara^d

^a*Instituto de Optica, CSIC, Serrano 121, 28006 Madrid, Spain*

^b*LMDH, Université Pierre et Marie Curie, UMR 7603 4 Place Jussieu, case 86, 75252, Paris Cedex 05, France*

^c*Instituto de Investigaciones en Materiales, Ciudad Universitaria, Circuito Exterior, 04510, México D.F., México*

^d*CBI, Universidad Autónoma Metropolitana Iztapalapa, Apdo. Postal 55-534, México D.F., México*

Abstract

Structural properties as a function of temperature of bismuth nanocrystals embedded in amorphous germanium thin films, synthesised by laser ablation are investigated by Raman spectroscopy and X-ray diffraction. In addition to temperature anharmonic effects, Raman spectroscopy results reveal a melting solidification hysteresis, which takes place below the melting point of bulk bismuth. Furthermore, preliminary X-ray diffraction results suggest that the nanocrystals change in structure upon heating until melting occurs. However, the nanocrystals recover their original structure once the sample is cooled at room temperature.

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1. Introduction

Nanocomposite materials containing nanocrystals (NCs) have novel optical, electrical and magnetic properties that depend on the nature and size of the NCs. These properties result, in fact, from the reduced dimension of the crystallites that can give rise to quantum confinement effects [1]. Regarding the thermodynamic aspects, a decrease of the melting point temperature of free standing NCs with respect to their bulk counterpart has been extensively observed [2]. In the case of clamped NCs temperature hysteresis effects have been reported [3].

In a previous work, the sensitivity of the Raman scattering response to size effects was used to study Bismuth NCs ranging from 2.3 to 23 nm [4]. In particular, an evolution of the optical modes of the crystalline phase was analysed and an attempt to relate the observed low frequency band with the theory of the normal modes of a vibrating sphere was reported. For this study, the Bi NCs embedded in amorphous Ge on a Silicon substrate were prepared by pulsed laser depo-

sition [5]. In the present work, the kinetics of the solid–liquid phase transition is followed using Raman spectroscopy and X-ray diffraction. Raman scattering is an interesting alternative since the Raman spectrum of a solid is strongly dependent upon temperature.

This nanocomposite system is particularly well suited to study thermal properties since, as pointed out in Ref. [6], embedding aggregates in a dielectric matrix present various advantages as avoiding any contamination and making the aggregates independent of each other. As a consequence, the successive cycles (fusion–solidification) do not exhibit any drift with time. Moreover, bismuth has a relatively low melting point (544 K) and Bi and Ge form a eutectic system with a low mutual solubility, thus facilitating the deposition of Bi in the form of pure isolated and unreacted crystals [5]. Upon cooling, the nano-drops crystallize again making a reversible system.

2. Experimental

2.1. Sample preparation

The sample is a thin nanocomposite film prepared by alternate pulsed laser deposition (ArF excimer laser at

*Corresponding author. Fax: +34-91-564-55-57.

E-mail address: haro@io.cfmac.csic.es (E. Haro-Poniatowski).

193 nm, with a pulse duration of 12 ns and 5-Hz repetition rate). To increase the amount of Bi NCs and, therefore, the Raman and X-ray diffraction signals related to them, a layered structure of Bi NCs was deposited and subsequently covered by a Ge continuous layer, this structure being repeated up to five times. The Bi NCs are oblate ellipsoids with two similar axes in thin film plane and a shorter axis in the film normal direction. In the present case, the mean diameter was 23 nm and the mean height 6 nm. A detailed description of the synthesis of the samples is given in Ref. [5].

2.2. Raman scattering measurements

Raman spectroscopy measurements were performed in vacuum using a Jobin-Yvon U1000 double monochromator. The 514.5-nm line of an Argon laser (Spectra Physics) was used as the excitation source at a power level of 50 mW. The diameter of the laser spot at the surface of the sample was of the order of 100 μm . Due to the low Raman signal (the weaker signals correspond to scattering by a few atomic layers), each spectrum was the result of the addition of several scans. Because of the low melting temperature of Bi, the black body emission in the visible range does not disturb the detection. For the temperature measurements, a homemade oven reaching temperatures up to 700 K was employed. The temperature was monitored by means of a thermocouple placed near the sample. The sample was heated step by step, once the desired temperature was reached; the system remained at that temperature at thermal equilibrium. The true temperature of the sample was measured from the Raman frequency shift of the optical phonon of the silicon substrate [7].

2.3. X-Ray measurements

X-ray diffraction patterns were obtained using a Siemens D500 diffractometer coupled to a copper anode tube whose K-alpha ($\lambda = 1.5405 \text{ \AA}$) radiation was selected with a diffracted beam monochromator. The samples were not powdered; they were just stuck to the sample holder in order to fulfil the Bragg condition. The high temperature measurements were made using a similar oven to the one described before with the same heating procedure. However, in this case the measurements were performed in air. Compounds were identified in the conventional way, i.e. with the JCPDS cards. To improve statistics the diffractograms were measured in continuous scan with a step size of 0.01° and a counting time of 0.6 s.

3. Results

In Fig. 1, the Stokes Raman spectra as a function of temperature are presented for increasing temperatures:

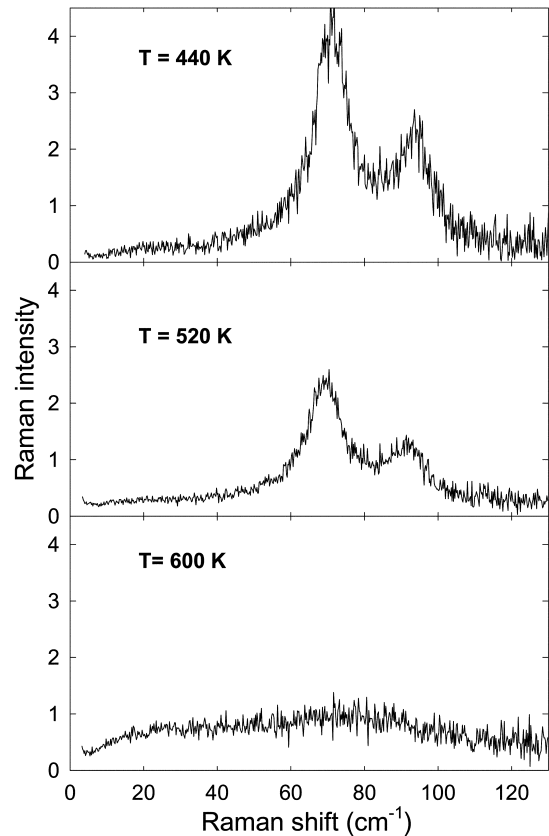


Fig. 1. Raman spectra of Bi NCs embedded in a-Ge as a function of temperature.

440, 520 and 600 K. At low temperature one observes the well-known modes E_g (70 cm^{-1}) and A_{1g} (97 cm^{-1}) of the Bi [4]. As expected, when the temperature increases, the peaks shift towards lower wave numbers because of anharmonic effects. Once the melting point is reached, the peaks disappear and are replaced by broad bands characterizing the liquid state. When the temperature decreases, the inverse process occurs and the crystalline peaks re-appear. However, this occurs at a significantly lower temperature than the temperature of melting.

In Fig. 2, the frequencies of the peaks are plotted as a function of temperature during the heating–cooling cycle. The optical phonons E_g (70 cm^{-1}) and A_{1g} (97 cm^{-1}) converge in one band (single frequency) as temperature increases (grey circles). One important feature that can be inferred from Fig. 2 is an hysteresis behaviour of the melting–solidification cycle [3,8]. From these results, one can assume that the difference between the melting and solidification temperatures is at least of the order of 50 K, however, more precise measurements need to be performed regarding this point.

The solid–liquid phase transition was also monitored by X-ray diffraction. Due to the small intensity of the signal, long accumulation times and a short angular

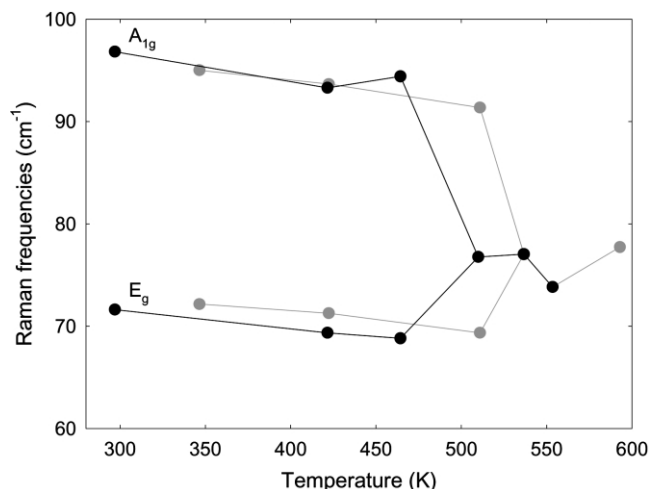


Fig. 2. Raman frequencies of the A_{1g} and E_g peaks as a function of temperature. A supercooling effect of at least 50 K is observed.

range were needed. In the range selected, two peaks characterizing crystalline bismuth appear, as seen in Fig. 3, the first one at 22.8° (003) and the second at 27.7° (012), the corresponding peak positions according to the JCPDS cards being 22.606° and 27.334° , respectively.

In Fig. 3, X-ray diffractograms are presented for increasing temperatures from ambient temperature to 620 K and then for decreasing temperature down to ambient. As one can observe, the effect of temperature on the structure of the NCs is striking. As the temperature increases, the structure changes; at 520 K the peak at 22.8° (003) markedly sharpens and increases in intensity, at 590 K practically all the features of the XRD pattern disappear indicating that the Bi has almost melted. Nevertheless, some very low intensity bands at the peak positions given above are still observable. At 620 K all the features in the XRD pattern have disappeared. Upon cooling to 520 K the peak reappears indicating that the nanoparticles have crystallised. Finally, at room temperature the starting XRD pattern has been recovered though less intense. To calculate the crystallite size distributions, the XTL-SIZE program [9,10] was used on the (012) and (003) peak profiles of the room temperature and the 520 K (heating) diffractograms. One finds from the size distributions that, upon increasing temperature, the crystals grow preferentially along the $\langle 003 \rangle$ as compared to the $\langle 012 \rangle$ direction. In the $\langle 003 \rangle$ direction many crystals having an average dimension of 13 nm appear while, in the $\langle 012 \rangle$ direction, the small crystals (3–6 nm) disappear at the expense of larger ones (7–12 nm). In summary, as temperature increases, the crystals growth is highly anisotropic inducing a modification of the crystals shape. When the sample is cooled again, the XRD pattern

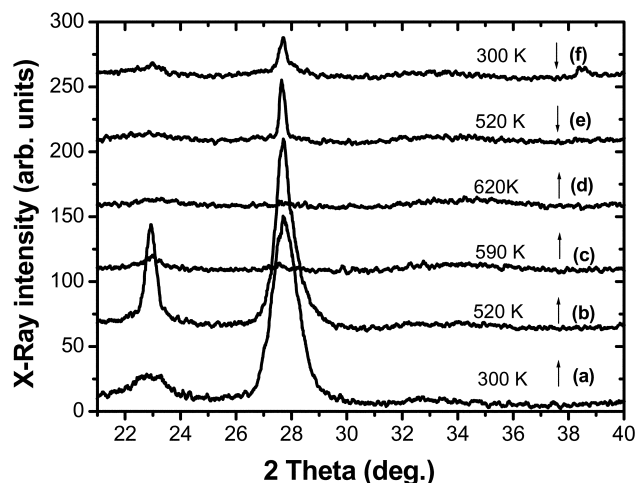


Fig. 3. X-Ray diffraction patterns as a function of temperature.

tends to recover, indicating a reversible transformation process.

4. Conclusions

The solid–liquid transitions of nanocrystalline bismuth, embedded in amorphous germanium, have been investigated by Raman spectroscopy and X-ray diffraction. At room temperature the system is composed of Bi nanocrystals embedded in an amorphous germanium matrix. At 590 K and above, the system is composed of Bi nano-drops embedded in an amorphous Ge matrix. The X-rays diffraction data allow confirming the phase transition from crystalline to liquid bismuth since, as expected, the diffraction peaks disappear. On the other hand, the same is observed by Raman Spectroscopy. However, in this case one would expect changes in the phonon density of states, since in going from solid to liquid the transverse waves disappear and only the longitudinal waves remain. Further studies need to be performed to analyse this particular aspect.

Regarding reversibility, after heating below 600 K, the Bi nanocrystals embedded in the amorphous Ge matrix are recovered. A melting–solidification temperature hysteresis of the order of 50 K is observed.

Acknowledgments

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References

- [1] C. Flytzanis, F. Hache, M.C. Klein, D. Ricard, Ph. Rousignol, in: E. Wolf (Ed.), *Progress in Optics XXIX*, Elsevier Science Publishers B.V, Holland, 1991, pp. 323–411.
- [2] R. Goswami, K. Chattopadhyay, *Appl. Phys. Lett.* 69 (1996) 910.
- [3] H.H. Andersen, E. Johnson, *Nucl. Instr. Meth. B* 106 (1995) 480.
- [4] E. Haro-Poniatowski, M. Jouanne, J.F. Morhange, M. Kanehisa, R. Serna, C.N. Afonso, *Phys. Rev. B* 60 (1999) 10080.
- [5] R. Serna, T. Missana, C.N. Afonso, J.M. Ballesteros, A.K. Petford-Long, R.C. Doole, *Appl. Phys. A: Mater. Sci. Process* A 66 (1998) 43.
- [6] R. Garrigos, R. Kofman, P. Cheyssac, M.Y. Perrin, *Europhys. Lett.* 1 (1986) 355.
- [7] M. Balkanski, R.F. Wallis, E. Haro, *Phys. Rev. B* 28 (1983) 1928.
- [8] R. Kofman, P. Cheyssac, A. Aouaj, Y. Lereah, G. Deutscher, T. Ben-David, J.M. Penisson, A. Bourret, *Surf. Sci.* 303 (1994) 231.
- [9] A.G. Alvarez, R.D. Bonetto, D.M.A. Guerin, S. Plastino, L. Rebollo Neira, *Powder Diffr* 2 (1987) 220.
- [10] D.M.A. Guerin, A.G. Alvarez, L. Rebollo Neira, S. Plastino, R.D. Bonetto, *Acta Crystallogr. A* 42 (1986) 30.