Deep-level-driven anomalous temperature dependence of lattice constants and energy gaps in $Mg_xZn_{1-x}Se$ and $Mg_xZn_{1-x}Se:Co^{2+}$ single crystals

Wha-Tek Kim

Department of Physics, Chonnam National University, Kwangju 500-757, Republic of Korea
(Received 27 October 1997; revised manuscript received 20 November 1998)

Pure $Mg_xZn_{1-x}Se$ (type C) single crystals were grown by the closed-tube sublimation method. $Mg_xZn_{1-x}Se$ (type D) and $Mg_xZn_{1-x}Se:Co^{2+}$ single crystals in which deep levels exist were grown by the chemical transport reaction method. The temperature dependence of the optical energy gaps of the $Mg_xZn_{1-x}Se$ (type C) single crystals fitted well with the Manoogian-Leclerc equation. However, the temperature dependence of the optical energy gaps of the $Mg_xZn_{1-x}Se$ (type D) and $Mg_xZn_{1-x}Se:Co^{2+}$ single crystals was anomalous in the temperature range of 10–70 K. This anomalous temperature dependence was analyzed as originating from a volume dilation effect due to deep-level defects. [S0163-1829(99)05608-8]

Energy gaps in most semiconductors except for Pb-chalcogenide semiconductors decrease slowly over a lower temperature range ($T<100$ K) and decrease abruptly in a higher range ($T>100$ K) with increasing temperature. This temperature dependence of energy gaps fits well with the Varshni empirical equation[1] and the Manoogian-Leclerc equation based on lattice dilation and electron-phonon interaction.[2]

Optical energy gaps of $AgGaS_2$,[3,4] $AgGa_{1-x}In_xSe_2$,[5] and $AgGaSe_2$ and $AgInSe_2$ (Ref. 6) single crystals show an anomalous temperature dependence in that the optical energy gaps increase over a lower temperature range with increasing temperature. It has been reported that the anomalous temperature dependence of the optical energy gaps becomes conspicuous when impurities with deep levels are doped into the single crystals.[7] However, the cause of the anomalous temperature dependence has not yet been identified clearly. In this study, in order to identify the anomalous property, notice is taken of the fact that the anomalous temperature dependence of the optical energy gaps is sensitive to the defects in the single crystals.

$Mg_xZn_{1-x}Se$ and $Mg_xZn_{1-x}Se:Co^{2+}$ single crystals were grown by the closed-tube sublimation method (CTSM) (Ref. 8) and the chemical transport reaction method (CTRM).[9] High-purity (99.999%) magnesium, zinc, and selenium were used as starting materials. CoI_2 (purity 99.9%) was introduced into the starting materials to dope the cobalt impurity in the $Mg_xZn_{1-x}Se:Co^{2+}$ single crystals. In order to prevent the magnesium from reacting chemically with the quartz ampules, high-purity BN tubes were used in growing the single crystals by CTSM, and the inner sections of the quartz ampules in which the starting materials were placed were coated with high-purity carbon in growing the single crystals by CRTM. Typical dimensions of the grown single crystals were $8\times7\times5$ mm. Two types (type C and type D) of the $Mg_xZn_{1-x}Se$ single crystals were obtained. The type-C single crystals were grown by CTSM and were colorless and transparent. The type-D single crystals were grown by CTRM and were somewhat opaque. The $Mg_xZn_{1-x}Se:Co^{2+}$ single crystals showed a pale brownish or greenish color.

The composition of the $Mg_xZn_{1-x}Se$ and $Mg_xZn_{1-x}Se:Co^{2+}$ single crystals was examined by energy dispersive x-ray microanalysis and electron probe microanalysis. The amount of cobalt doped as an impurity was about 0.02–0.75 mol%. The crystal structures and the lattice constants of the single crystals were determined from the x-ray diffraction patterns measured over the temperature range of 10–300 K using an x-ray diffractometer (Rigaku, DMAX2000) equipped with a cryogenic system. The values of the lattice constants were obtained from the mean square calculated from ten or more samples. The margins of error were within ±0.0003 Å. Deep levels of the single crystals were determined from thermally stimulated current and photoinduced current transient spectroscopy.[10] Optical-absorption spectra were measured over the temperature range of 10–300 K by using a uv-vis-nir spectrophotometer (Hitachi, U-3501) equipped with a cryogenic system (Air Product, CSA-202B). The optical energy gaps of the single crystals were deduced from the optical-absorption spectra measured near the fundamental absorption edge.

The $Mg_xZn_{1-x}Se$ (type C and D) and $Mg_xZn_{1-x}Se:Co^{2+}$ single crystals crystallized into a zinc-blende structure in the composition range of $x=0.00-0.18$ and a wurtzite structure in the composition range of $x=0.20-0.50$. The lattice constants of the $Mg_xZn_{1-x}Se$ (type D) single crystals were greater than those of the $Mg_xZn_{1-x}Se$ (type C) single crystals, and those of the impurity-doped $Mg_xZn_{1-x}Se:Co^{2+}$ single crystals were much greater than those of the $Mg_xZn_{1-x}Se$ (type D) single crystals at each composition.

The optical energy gaps of the $Mg_xZn_{1-x}Se$ (type C)

TABLE I. Deep energy levels of the $Mg_xZn_{1-x}Se$ (type D) single crystals.

Material	Crystal structure	Electron D_1	D_2	D_3	Hole A_1	A_2	A_3
ZnSe	zinc blende	0.22	0.30	0.40	0.19	0.45	
$Mg_{0.1}Zn_{0.9}Se$	zinc blende	0.13	0.27	0.50	0.19	0.45	
$Mg_{0.2}Zn_{0.9}Se$	wurtzite	0.17	0.29	0.54	0.20	0.46	0.62
$Mg_{0.3}Zn_{0.9}Se$	wurtzite	0.29	0.36	0.54		0.47	0.62
$Mg_{0.4}Zn_{0.9}Se$	wurtzite		0.37	0.54		0.47	0.62
$Mg_{0.5}Zn_{0.9}Se$	wurtzite	0.13		0.54		0.48	0.62

single crystals at 300 K increased from 2.785 eV to 3.122 eV with an increase of composition x from 0.0 to 0.50. The optical energy gaps of the $Mg_xZn_{1-x}Se$ (type D) single crystals at 300 K increased from 2.534 eV to 3.186 eV with an increase of composition x from 0.0 to 0.50. The optical energy gaps of the $Mg_xZn_{1-x}Se:Co^{2+}$ single crystals at 300 K increased from 2.520 eV to 3.037 eV with an increase of composition x from 0.0 to 0.50. Taking into account the optical energy gaps of $Mg_xZn_{1-x}Se$ single crystals grown by the high-pressure Bridgman method[11] and of $Mg_xZn_{1-x}Se$ alloys with a zinc-blende structure grown by molecular beam epitaxy,[12] these optical energy gaps are reasonable.

There were no deep levels and strong blue emissions observed in the $Mg_xZn_{1-x}Se$ (type C) single crystals. Deep

donor and acceptor levels were identified in the $Mg_xZn_{1-x}Se$ (type D) single crystals, and are listed in Table I. In the $Mg_xZn_{1-x}Se:Co^{2+}$ single crystals, the energy levels of the Co^{2+} ion sited in T_d symmetry exist as deep levels in the single crystals.[13]

Figure 1 shows the temperature dependence of the optical energy gaps of the $Mg_xZn_{1-x}Se$ (type C and D) and $Mg_xZn_{1-x}Se:Co^{2+}$ single crystals at compositions $x=0.1$ and 0.2 with the zinc-blende and wurtzite structures, respectively. The temperature dependency of the optical energy gaps of the $Mg_xZn_{1-x}Se$ (type C) single crystals matched well with the following theoretical Manoogian-Leclerc equation,[2] which consists of two parts volume dilation due to thermal expansion and the electron-phonon interaction:
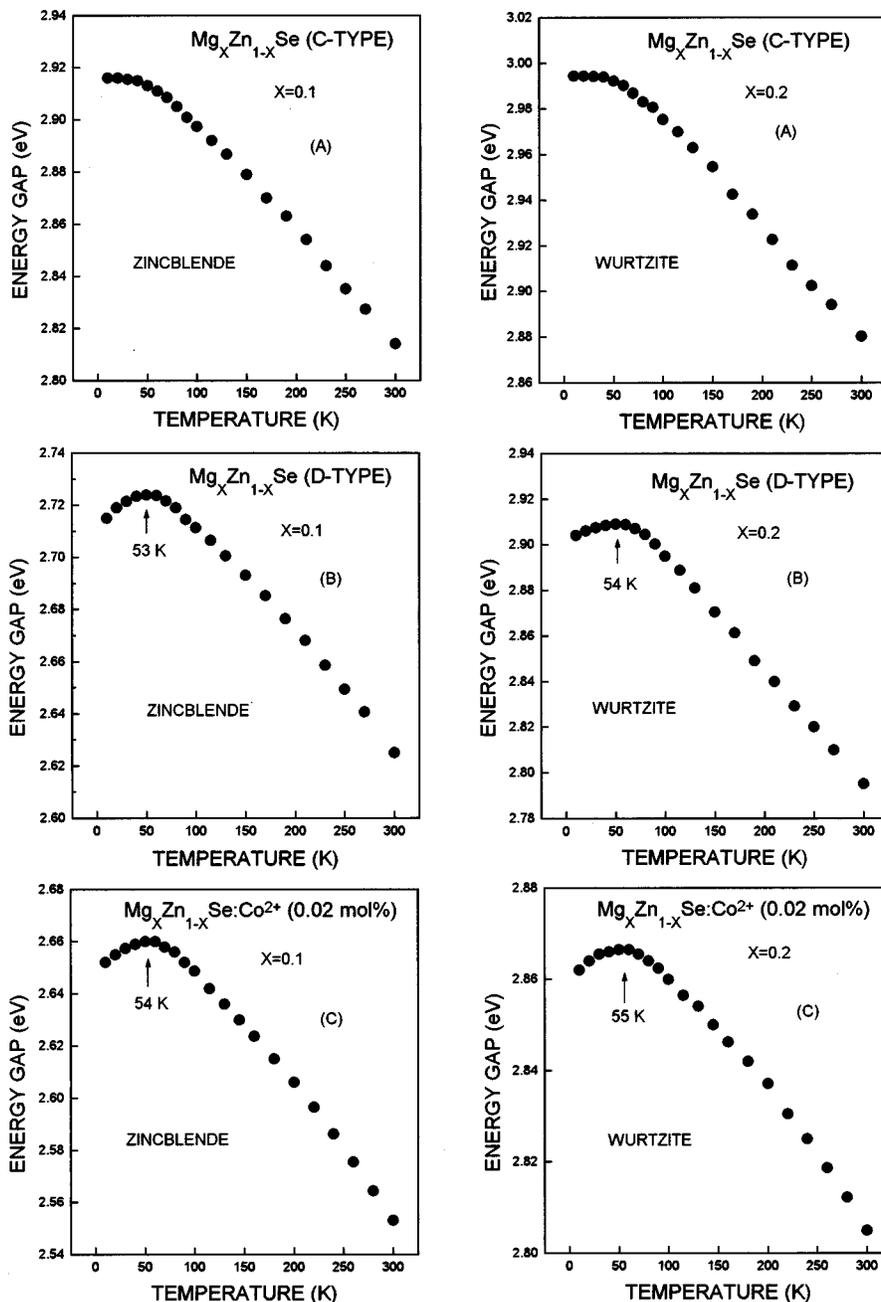
FIG. 1. Temperature dependence of optical energy gaps of $Mg_xZn_{1-x}Se$ (type C and D) and $Mg_xZn_{1-x}Se:Co^{2+}$ single crystals.
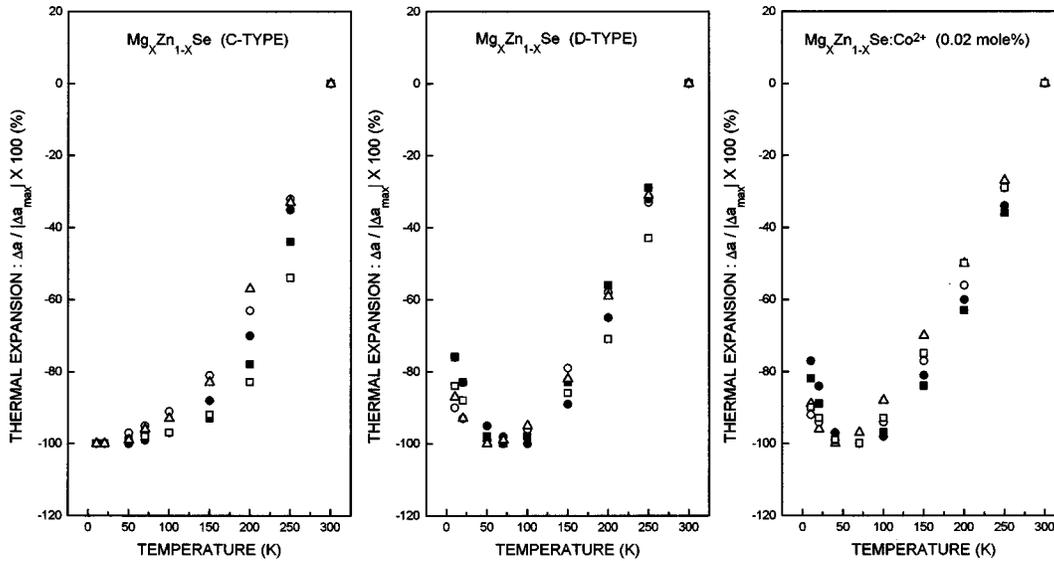
FIG. 2. Temperature dependence of linear thermal expansion of $Mg_xZn_{1-x}Se$ (type C and D) and $Mg_xZn_{1-x}Se:Co^{2+}$ single crystals ($\triangle$: $x=0.1$, $\bullet$: $x=0.2$, $\square$: $x=0.3$, $\bigcirc$: $x=0.4$, $\square$: $x=0.5$).

$$\Delta E = E_g(0) - E_g(T)$$

$$= UT^S + V\Theta\left(\coth\frac{\theta}{2T} - 1\right),$$ (1)

where ΔE is the decreased energy as temperature increases, $E_g(0)$ and $E_g(T)$ are the energy gaps at 0 K and T K, and U, S, V, and Θ are coefficients independent of temperature.

The temperature dependence of the optical energy gaps in the $Mg_xZn_{1-x}Se$ (type D) and $Mg_xZn_{1-x}Se:Co^{2+}$ single crystals at compositions $x=0.1$ and 0.2 was anomalous. The optical energy gaps increased when the temperature was raised from 10 K to 53~55 K, and decreased abruptly with an increase in the temperature to 300 K. The temperature dependence of the optical energy gaps in the temperature range of 10 K to 53~55 K could not match with the Manoogian-Leclerc equation[2] and the Varshni equation.[1] This anomalous temperature dependence was observed in the other $Mg_xZn_{1-x}Se$ (type D) and $Mg_xZn_{1-x}Se:Co^{2+}$ single crystals at compositions $x=0.3$, 0.4, and 0.5.

The temperature dependence of the lattice constant a of the $Mg_xZn_{1-x}Se$ (type C and D) and $Mg_xZn_{1-x}Se:Co^{2+}$ single crystals is shown in Fig. 2. The values of $\Delta a/|\Delta a_{max}| = (a_{300\,K}-a)/(|a_{300\,K}-a_{min}|)$ at each composition x are used as thermal expansion, where $a_{300\,K}$ is the lattice constant a at 300 K and a_{min} is the minimum value of the lattice constant a. The lattice constant a of the $Mg_xZn_{1-x}Se$ (type C) single crystals increased slowly when the temperature of the single crystals is raised from 10 K to 100 K, and increased abruptly with an increase of the temperature to 300 K. The lattice constant c of the type-C single crystals with the wurtzite structure showed a temperature dependence similar to that of the lattice constant a. On the other hand, the lattice constant a of the $Mg_xZn_{1-x}Se$ (type D) single crystals decreased with increasing temperature form 10 K to 50~75 K and increased with increasing temperature to 300 K. This anomalous temperature dependence

of the lattice constant a was also observed in the $Mg_xZn_{1-x}Se:Co^{2+}$ single crystals.

Anomalous temperature dependence of lattice constants has been reported for Si, HgTe, CdTe, and $Hg_xCd_{1-x}Te$ single crystals.[14] It has been analyzed that heavy substitutional or interstitial impurities may well produce an increase in the magnitude of the thermal expansion coefficient at low temperatures. In GaS, GaSe, and InSe single crystals with layer structure, negative linear expansion was observed in a temperature range less than 50 K when thermal expansion was measured in the parallel direction with the c axis.[15] It was reported that the anomalous temperature dependence of the optical energy gaps of GaS and GaSe single crystals was observed in the lower temperature range in which the negative linear expansion appeared.[16]

In compound or alloyed semiconductors with deep-level defects, lattice relaxation occurs due to the fluctuation of the atom arrangement around the defects.[17,18] This lattice relaxation affects the thermal expansion of the semiconductor. The temperature dependence of the lattice heat conductivity in the lower temperature range is determined by the temperature dependence of the heat capacity, which is affected by the thermal expansion.[19] Therefore, it is considered that the thermal expansion is related to the lattice heat conductivity. In materials with defects such as a synthetic sapphire, a sodium fluoride, and a germanium, the temperature dependence of the lattice heat conductivity has peaks in the temperature range of 40–50 K, and the peaks move to a higher temperature when the number of defects increases.[19,20] Hence, the anomalous temperature dependence of the lattice constants in the lower temperature range, which was observed for the $Mg_xZn_{1-x}Se$ (type D) and $Mg_xZn_{1-x}Se:Co^{2+}$ single crystals, can be analyzed as appearing because the lattice heat conductivity in the single crystals with the deep-level defects has a peak at low temperature.

In general, the energy gap of a semiconductor increases when the lattice constant decreases by volume shrinkage and decreases when the lattice constant increases by volume di-

lation. Therefore, the anomalous temperature dependence of the optical energy gaps of the $Mg_xZn_{1-x}Se$ (type D) and $Mg_xZn_{1-x}Se:Co^{2+}$ single crystals shown in Fig. 1 can be analyzed as appearing in relation with the anomalous temperature dependence of the lattice constants.

Few studies have been reported on the thermal expansion of ternary semiconductors so far. Thus the results of this study cannot be compared with others. However, the results can be convincing from the fact that the anomalous temperature dependence of optical energy gaps of GaS and GaSe single crystals with layer structure is caused by negative linear expansion.[15,16]

In conclusion, the anomalous temperature dependence of the optical energy gaps observed in the $Mg_xZn_{1-x}Se$ (type D) and $Mg_xZn_{1-x}Se:Co^{2+}$ single crystals is considered to be due to the anomalous temperature dependence of the lattice constants originating from the deep-level defects existing in the single crystals. The anomalous temperature dependence of the optical energy gaps can be explained by a division: the volume dilation effect and the electron-phonon interaction effect. The effect of the electron-phonon interaction on the temperature dependence of the optical energy gaps is smaller than that of the volume dilation at a low-temperature range but becomes greater and greater at a higher-temperature range. Thus, it is considered that the anomalous temperature dependence of the optical energy gap occurring in a low-temperature range is more dependent on the volume dilation effect. On the other hand, considering the variation of the optical energy gaps in the temperature range of 10–300 K, the variation due to the volume dilation effect is much smaller than that due to the electron-phonon interaction effect. It can, therefore, be seen that the optical energy gap variation in the temperature range in which the anomalous temperature dependence of the optical energy gaps occurs is small, as shown in Fig. 1.

[1] Y. P. Varshni, Physica (Amsterdam) **43**, 149 (1967).

[2] A. Manoogian and A. Leclerc, Phys. Status Solidi B **92**, K23 (1979).

[3] P. W. Yu, W. J. Anderson, and Y. S. Park, Solid State Commun. **13**, 1883 (1973).

[4] J. P. Leyris and J. P. Aicardi, Phys. Status Solidi A **92**, 279 (1985).

[5] Suk-Ryong Hang and Wha-Tek Kim, Phys. Rev. B **27**, 5129 (1983).

[6] V. A. Aliyev, G. D. Guseinov, F. I. Mamedov, and L. M. Chapanova, Solid State Commun. **59**, 745 (1986).

[7] Suk-Ryong Hahn, Wha-Tek Kim, Yong-Guen Kim, and Hyung-Gon Kim, J. Appl. Phys. **69**, 7797 (1991).

[8] A. M. Mancini, C. Manfredotti, R. Piccolo, and A. Rizzo, J. Phys. Chem. Solids **38**, 665 (1977).

[9] Yang-Lae Lee and Wha-Tek Kim, Phys. Rev. B **50**, 10 672 (1994).

[10] Ho-Jun Song, Sang-Hyun Yun, and Wha-Tek Kim, Solid State Commun. **94**, 225 (1995).

[11] F. Firszt, H. Meczynska, B. Sekulska, J. Sxatkowski, W. Paszkowicz, and J. Kachniarz, Semicond. Sci. Technol. **10**, 197 (1995).

[12] B. Jobst, D. Hommel, U. Lunz, T. Gerhard, and G. Landwehr, Appl. Phys. Lett. **69**, 97 (1996).

[13] Sang-An Park, Ho-Jun Song, Duck-Tae Kim, Hyung-Gon Kim, Moon-Seog Jin, Chang-Dae Kim, Chang-Sun Yoon, and Wha-Tek Kim, Semicond. Sci. Technol. **13**, 1011 (1988).

[14] O. Caporaletti and G. M. Graham, Appl. Phys. Lett. **39**, 338 (1981).

[15] G. L. Belenkii, E. Yu. Salaev, R. A. Suleimanov, N. A. Abdullaev, and V. Pa. Shteinshraiber, Solid State Commun. **53**, 967 (1985).

[16] G. L. Belenkii, E. Yu. Salaev, R. A. Suleimanov, and N. A. Abdullaev, Solid State Commun. **47**, 263 (1983).

[17] H. Kukimoto, C. H. Henry, and F. R. Merritt, Phys. Rev. B **7**, 2488 (1973).

[18] H. Kukimoto, Semicond. Insul. **5**, 337 (1983).

[19] G. I. Epifanov, *Solid State Physics* (Mir, Moscow, 1977), p. 129.

[20] C. Kittel, *Introduction to Solid State Physics* (Wiley, New York, 1971), p. 231.