Improving the Optical Properties of Potassium Chloride Crystals by Doping Diamond Nanoparticles

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Research Article

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Abstract

In this work, the growth and characterization of potassium chloride crystals containing diamond nanoparticles has been performed. The crystals were grown by the Czochralski method and the doped samples contained 0.5, 1 and 1.5% impurities of diamond nanoparticles. The crystals were characterized by X ray diffraction (XRD), Fourier transform infra-red spectroscopy (FTIR), scanning electron microscopy (SEM), etching and thermoluminesence (TL). The XRD analysis shows the most of the nanodiamonds are still in single crystal form. FTIR demonstrates the composed crystals are transparent in IR range (transmission ~ 87%). The etching analysis reveals a crystal dislocation in order of 10^5 for the samples. Examination of thermoluminescence properties of crystals by gamma irradiation with doses of 10, 80 and 300 Gy showed that the sample with 0.5% doped ND had the best glow curve, but for the dose of 1000 Gy, the sample with 1% doped had the best curve.

1. Introduction

Detonation nanodiamond (ND) was discovered in 1963, but for several reasons was known only among a small number of scientists until the turn of the century [1]. Nano-diamond, prepared by the detonation technique, has been widely used as an additive to improve the performance of various materials [2]. The high dispersibility of the nanodiamond powder makes it possible to form a high density of nano-inclusions in their matrixes [3]. KCl alkali halide crystal is a kind of transparent crystals in vast range of electromagnetic spectrum [4]. Many researchers [5–8] did Studying and characterization of doped KCl crystals. Amazing optical properties of KCl as well as its low price caused to broad using of it in thermoluminescence, dosimetry and medical purposes [9]. This crystal can be used specially as an optical window in CO_2 laser with power more than 10 kw [10], because it has got low absorption in wavelength 10.6 μm in IR confine [11]. One of the KCl crystal disadvantageous is its low mechanical hardness [12, 13].The hardness is an important mechanical property of materials. It was defined as the resistance offered by a given material to external mechanical action endeavouring to scratch, abrade, indent, or affect in any other way its surface. Hardness measures a material's ability to resist deformation and is determined by elastic stiffness and plastic resistance. Because elastic stiffness and plastic deformation are all closely related to the resistant force of the chemical bond, it is suggested that the hardness of an ideal solid is mainly determined by the nature of its chemical bonding. However, hardness is too complex to be described by first principles. Generally speaking, hardness depends strongly on plastic deformation, which is related to the creation and motion of dislocations [14]. In a covalent crystal, bonding is highly stereospecific and dislocation energy depends strongly on its position. Regardless of details, a basic fact remains that, in order to plastically shear such a crystal, electron-pair bonds must first be broken and then remade, resulting in two unpaired electrons when an atomic shear process is half completed. Previously, we show that doping diamond nanoparticles in KCL crystals increases the mechanical hardness of the crystals [13].

2. Experimental

KCl powder with 99.99% purity and diamond nanoparticles with an average size of 80 nm were used for the growth of composite crystals. 100 g of KCl powder and 0.05, 0.01 and 0.15 g of ND powder were grown, separately. The materials were put inside a platinum crucible (inside diameter 11 cm, depth 6 cm, weight 125 g). Then, crucible was put into Czochralski furnace (inside diameter 155 mm, inside depth 300 mm, maximum temperature 1200 ˚C). A fine grain of pure KCl was connected to lifting- rotating system as seed for nucleation. In order to evaporate the water in the material, the furnace temperature is gradually increased. After that, the temperature was kept constant at 780 ˚C. It took 30 minutes for the material to melt. Then, the molten material was connected to the grain and at the same time the rotating lifting system started working. Lifting speed was 8 mm/h and rotating angular velocity was 1 turn/h. In order to increase the diameter of the crystal, after the neck of the crystal grew to about 3 mm, the temperature was reduced by 2 degrees Celsius every 15 minutes. The crystal growth process stopped after 230 minutes, after which the operation to reduce the neck diameter and gradually cut the crystal began. The cutting operation began with an increase in temperature of 5 ˚C. Then, after 15 minutes, at the same time as the temperature increased by 2 ˚C, the lifting speed decreased to 6 mm/h. 60 minutes later, the temperature increased by 3 ˚C and 15 minutes after doing so, the temperature increased by 5 ˚C and at the same time with this increase in temperature, the lifting speed was increased to 10 mm/h. The crystal took about 10 minutes in the last condition to separate on its own from the molten material. Finally, the furnace was turned off to allow the crystal to cool gradually. Figure 1 shows the KCl:(1.5%)ND crystal.

The XRD analysis was done by ITALSTRUCTURE system ADP2000 (Its accuracy is about 0.001). The ND concentrations less than 1% are not distinguishable by that equipment. Then, the XRD patterns of the pure and the KCl + 1.5% ND were analysed. The distribution of the ND nanoparticles inside the KCl crystals was investigated by environmental scanning electron microscope (ESSEM), Philips model XL30. For the etching analysis, the sample pieces were cut and washed with dilute HF + HCl solution for a few minutes to exaggerate fine crystalline defects. The samples were then washed with acetone and dried by hot air flow. A microscope with magnification ~ 500 and the films with sensitivity ~ 400 were used to image the surface of the etched samples. The FTIR was done by ELMER PERKIN Spectrum 400 equipment. The TL was done by irradiation of four samples (pure KCl, KCl + 0.5% ND, KCl + 1% ND and KCl + 1.5% ND) by ^{60}Co source with 10, 80, 300G and 1KG doses, separately. After that, by thermoluminescence dosimeter reader (Harshaw TLD model 4000), the samples were read.

3. Results And Discussion

The XRD patterns of the pure and 1.5% doped samples are shown in Figs. 2 and 3, respectively. The samples are still single crystals and doping the NDs host crystal does not effect on its single crystal properties. For using, the crystal in optical systems single crystals is more applicable than polycrystalline. As seen in figures, the important planes (200) and (400), in doped crystal, are not shifted and they are parallel.

In crystal growth mechanism, it is very important to distribute the impurity in based crystal uniformly. It is simple in cases of ionic additives because in the melt state, ionic bonding are broken and external ions can sit easily instead of original ions of the crystal lattice. In this research as it is clear, ND particles have a complete structure, so observing their placement in host environment that has considerably different structure can be helpful for modification of crystal growth methods. Pieces of KCl with different amounts of ND crystal were cut randomly and observed by ESEM. The ESEM images of the sample are shown in the Figs. 4–6. Figure 4 depicts KCl + 0.5% ND sample. In the figure, we can see a nearly smooth distribution of the NDs inside the host crystal. The ND cluster size varies between 133 to 421 nm. Figure 5 shows KCl + 1.0% ND sample. The distribution of the NDs is not smooth as the KCl + 0.5% ND sample and the ND cluster size changes between 53.4 to 107 nm. In the Fig. 6, we have a smooth distribution of the NDs with a size range from 295 to 502 nm. It has observed a little agglomeration of ND particles that is natural, because surface adhesionin ND particles is strong and they tend to stick together.

The results of the etching analysis are shown in Figs. 7–10. Based on mentioned figures, the surface dislocation of the samples are collected in the Table 1.

Table 1
KCl Samples Dislocation Surface Densities

Dislocation Surface Density(cm^{-2})	**Crystal**
$10^5 \times 3.0$	KCl (Pure)
$10^5 \times 4.5$	KCl + 0.5% ND
$10^5 \times 6.0$	KCl + 1.0% ND
$10^5 \times 8.8$	KCl + 1.5% ND

The KCl crystal is transparent in the IR range. Therefore, this crystal can be utilized as an optical window for the lasers working in the IR range (for example CO_2 laser). The FTIR analysis was done on the KCl + 1.5 % ND sample. The selected sample had the most ND impurity and the effect of the impurity on its transparency was more than other samples. Figure 11 shows the FTIR transmission spectrum for the KCl + 1.5 % ND sample. As it can be seen, the transmission is ~ 87.4%. This transmission shows the sample is nearly transparent in the IR range. Before, utilizing of the KCl crystal as a laser window had a limitation due to damaging the crystal by beam collision. One way to solve the problem was the crystal coating in order to increase the hardness and the crystal's lifetime. Unfortunately, that way was not economic. Considering the results of the harness analysis and the FTIR spectrum shows ND doping into the KCl crystal is the better method to overcome the problem.

The samples (pure KCl, KCl + 0.5% ND, KCl + 1% ND and KCl + 1.5% ND) were irradiated by gamma ^{60}Co source with 10, 80 and 300 Gy as well as 1kGy doses, separately. After irradiation, the colour of the samples changed to violet. Then, by TL reader the sample were characterized. The results are collected in Figs. 12–15.

The results are compared with the thermoluminesence curve of LiF:Mg,Ti reference dosimeter (known commercially as TLD100). Its significant dosimeteric peaks occur in temperature range between 160–260° C. For all samples the TL intensity of the ND doped KCl is stronger than pure crystal. In the Fig. 16, we can see the under curve area for the KCl + 0.5% ND sample is the greatest one. Therefore, in 10Gy irradiation dose, the best sample is the KCl + 0.5% ND sample. Its TL significant peaks occur on 160 and 240 ° C the operation temperature range is 100–300° C. In the Fig. 17 (80 Gy irradiation), the KCl + 0.5% ND sample has the best quality for TL and its significant peak appears on 180° C and the operation temperature range is 100–260° C. Again, in the operation temperature range between 100–200° C, the KCl + 0.5% ND sample shows the best quality in comparison with the other samples (Fig. 18). The significant peak occurs on 180° C. In the Fig. 19, the best TL quality belongs to KCl + 1% ND sample. Its operation temperature range and significant peak are 100–250 ° C and 160° C, respectively. As a result, for low irradiation doses 0.5% ND impurity and for high doses 1% ND impurity are proper for TL dosimetery.

4. Conclusion

The KCl crystals with various ND impurities were grown by Czochralski method. The ND doping percentages were 0, 0.5, 1 and 1.5. The increasing of the doping leads to growth of the lattice dislocations. Due to more dislocations, hardness of the crystal increases. The transparency of the doped crystals were comparable with pure crystals. The order of the dislocations was ~ 10^5. Those properties and better mechanical hardness of the doped crystals make them suite crystals for the optical applications. Significant improvement in TL characteristics of the ND doped KCl crystals makes them as a proper choice for vast gamma range for dosimetry.

5. References

1. Osawa, E.: Pure Appl. Chem. **80**(7), 1365 (2008)
2. Chen, Q., Yun, S.: Mater. Res. Bull. **35**, 1915 (2000)
3. Cheng, C.H., Zhang, H., Zhao, Y., Feng, Y., Rui, X.F., Munroe, P., M.Zeng, H., Koshizuka, N., Murakami, M.: Supercond. Sci. & Technol. **16**(10), 1183 (2003)
4. Pan, S., Jiang, B., Jiang, X., Qiu, J., Zhu, C.: J. Crys. Grow. **263**, 648 (2004)
5. Mele´ndreza, R., Pe´rez-Salasa, R.: Appl. Phys. Let. **68**(24), 3398 (1996)
6. Bangaru, S., Muralidharan, G.: Phys. B **407**, 2185 (2012)
7. Tanır, G., Bölükdemir, M.H., Çatlı, S., Tel, E.: Rad. Measur. **42**, 29 (2007)
8. Bhujbal, P.M.: and S. J. Dhoble. Luminescence **28**(6), 879 (2013)
9. Scott, B.F., Stovell, J.E.: Opt. Technol. **1**(4), 224 (1968)

10. Atanassov, G.A., Ivanov, V.A., Kotlikov, E.N., Popov, D.N., Shifrin, B.F.: Thin Solid Films **213**, 251 (1992)
11. Jayakumari, K., Mahadevan, C.: J. Phys. Chem. Solids **66**, 1705 (2005)
12. Harris:Durable, D.C.: Infra. Phys. & Technol. **39**, 185 (1998)
13. Dehghanpour, H.R., Nourazar, S.: Modares Mechanical Engineering **17**(11), 380 (2018)
14. Haines, J., Leger, J.M., Bocquillon, G.: Annu. Rev. Mater. Res. **31**, 1 (2001)

Figures

Figure 1

the grown KCl crystal with 1.5% nanodiamond doping

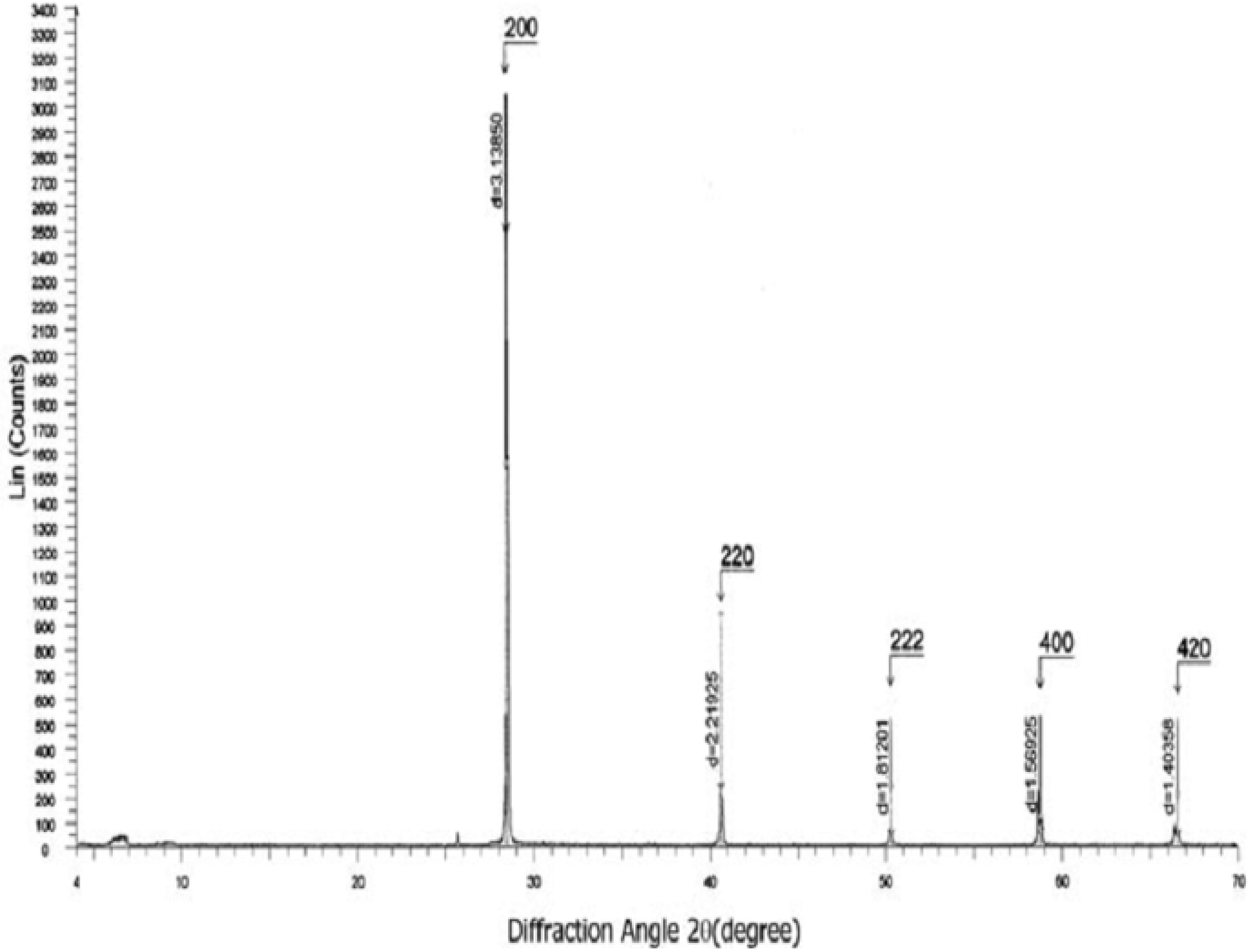

Figure 2

XRD pattern of the pure KCl crystal

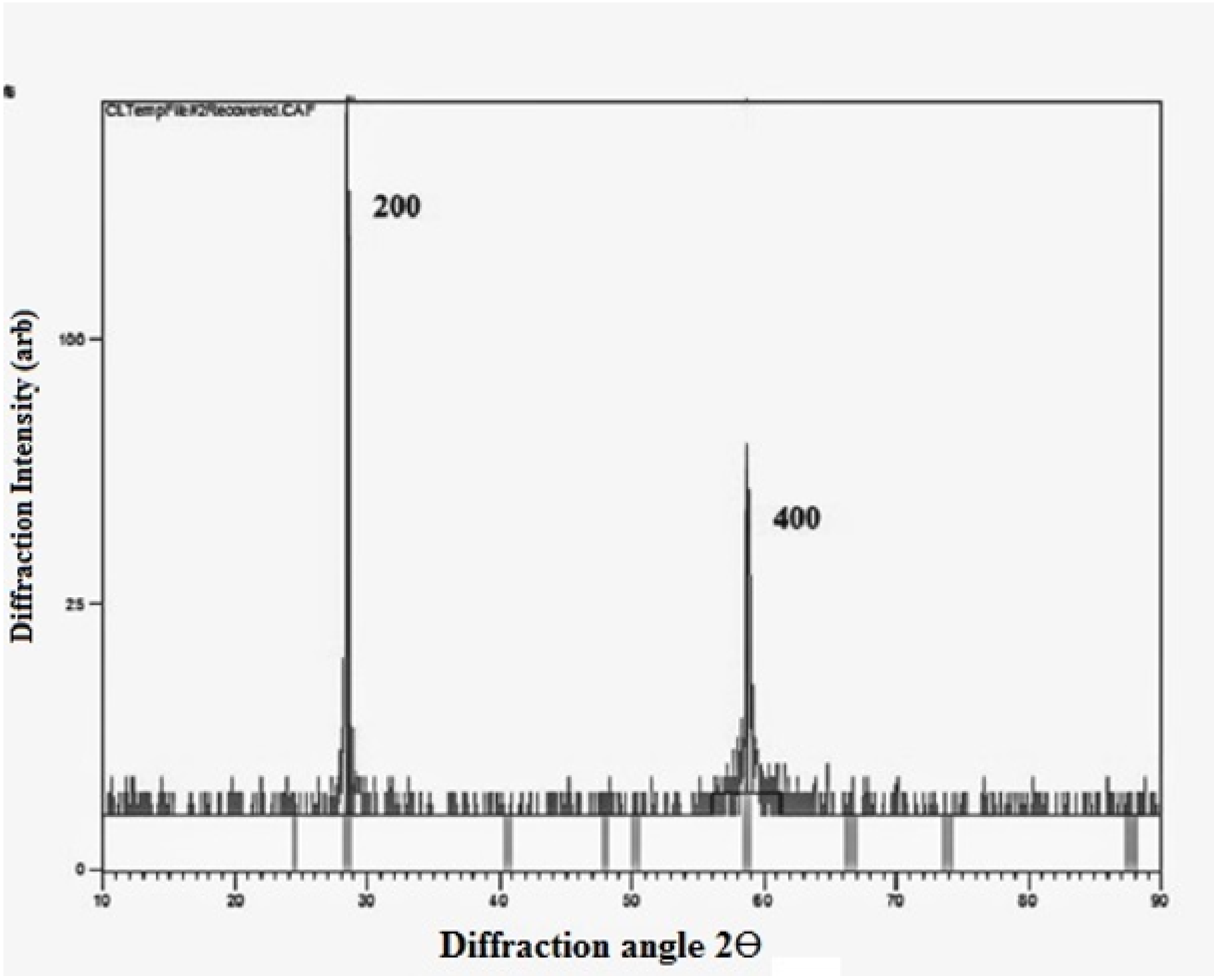

Figure 3

XRD pattern of the KCl crystal doped with 1.5% ND impurity

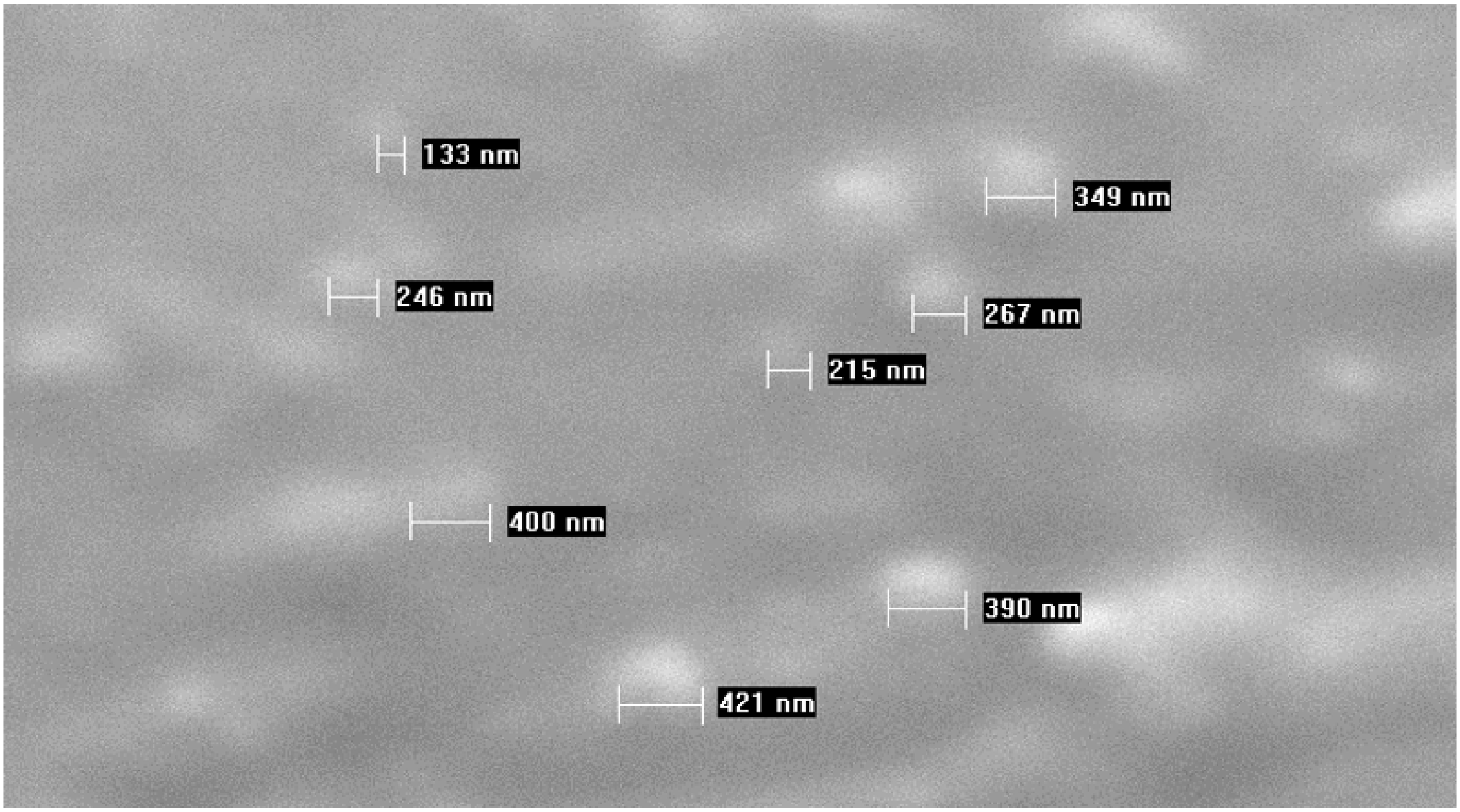

Figure 4

ESEM image of the KCl+ 0.5% ND sample

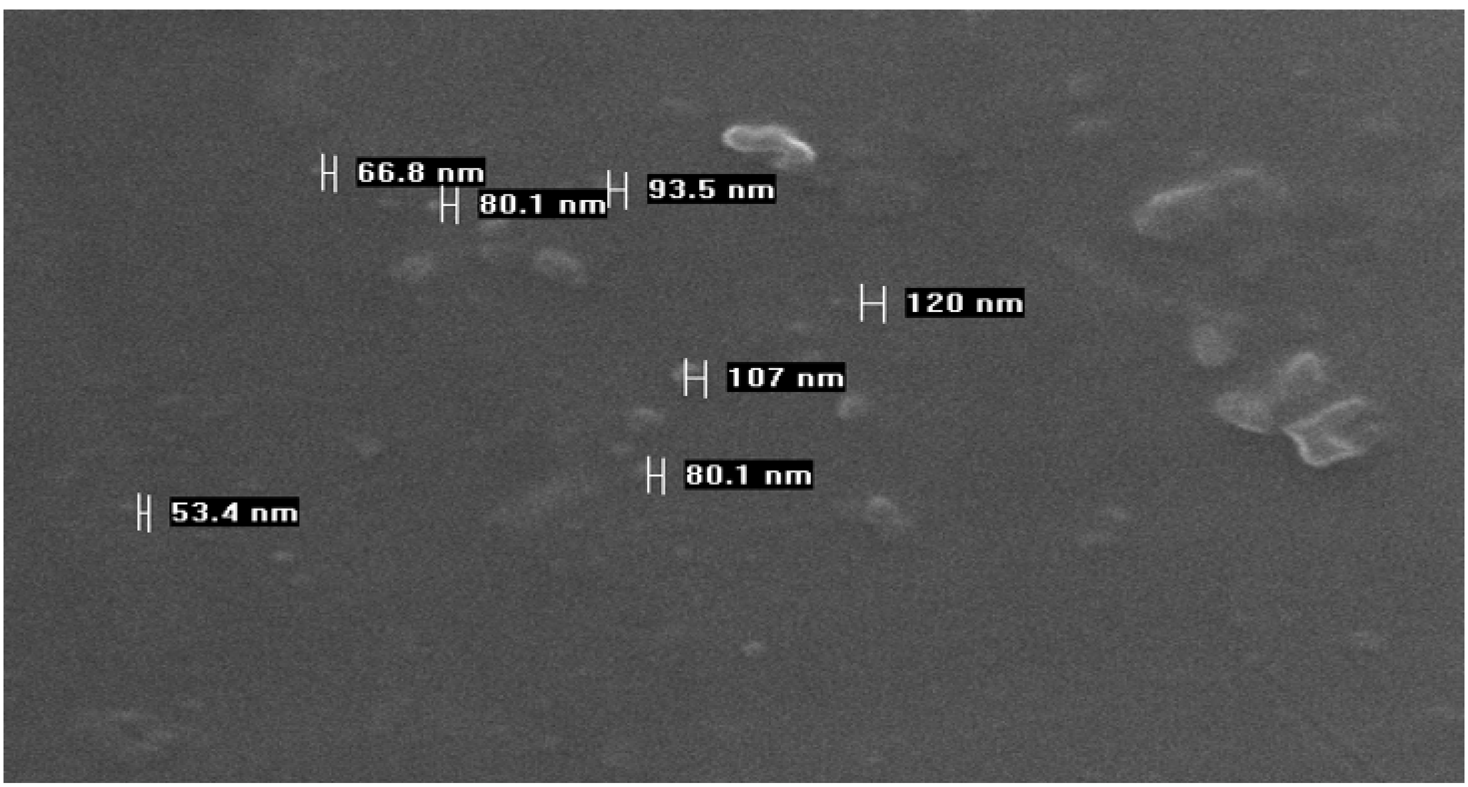

Figure 5

ESEM image of the KCl+ 1.0% ND sample

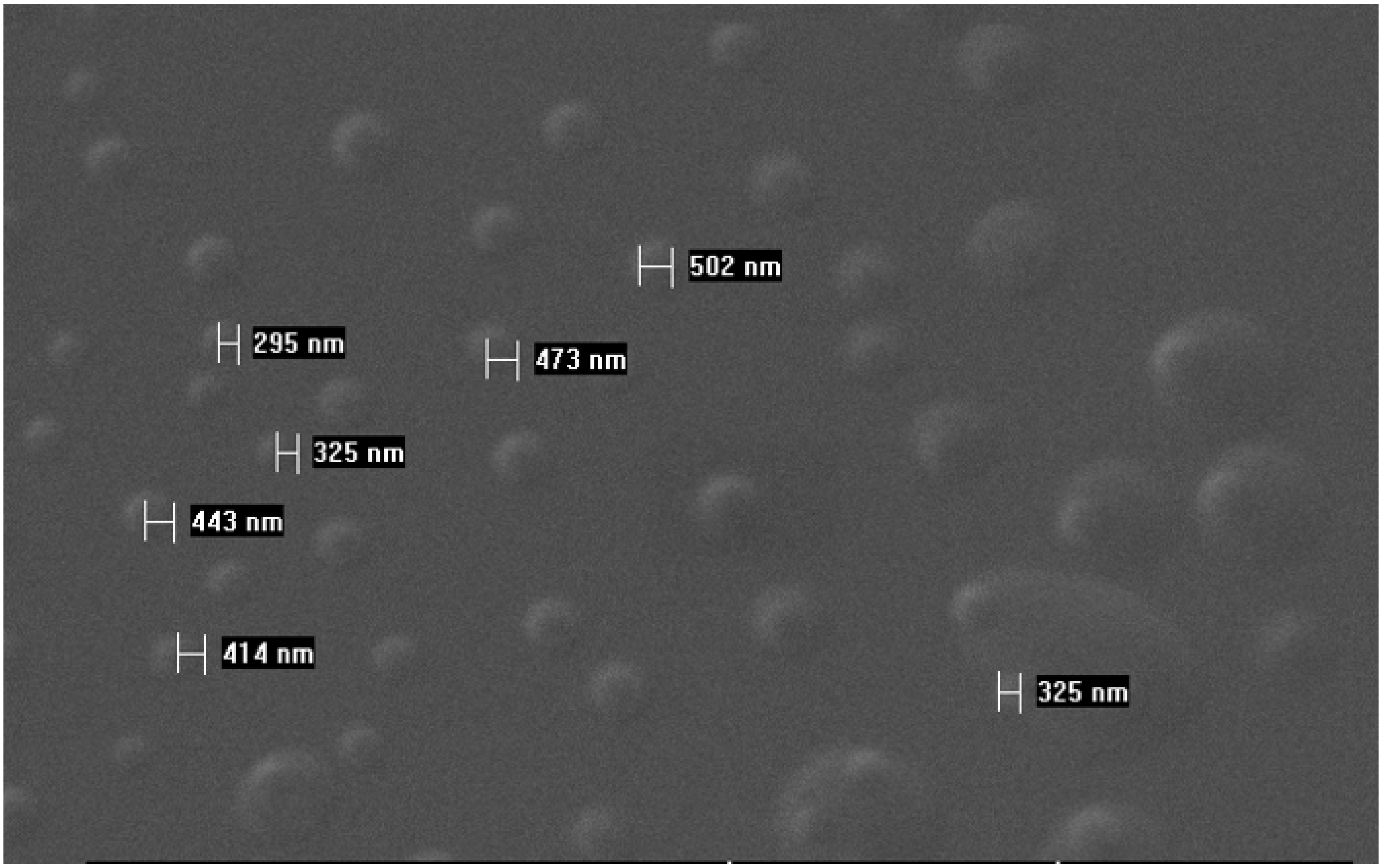

Figure 6

ESEM image of the KCl+ 1.5% ND sample

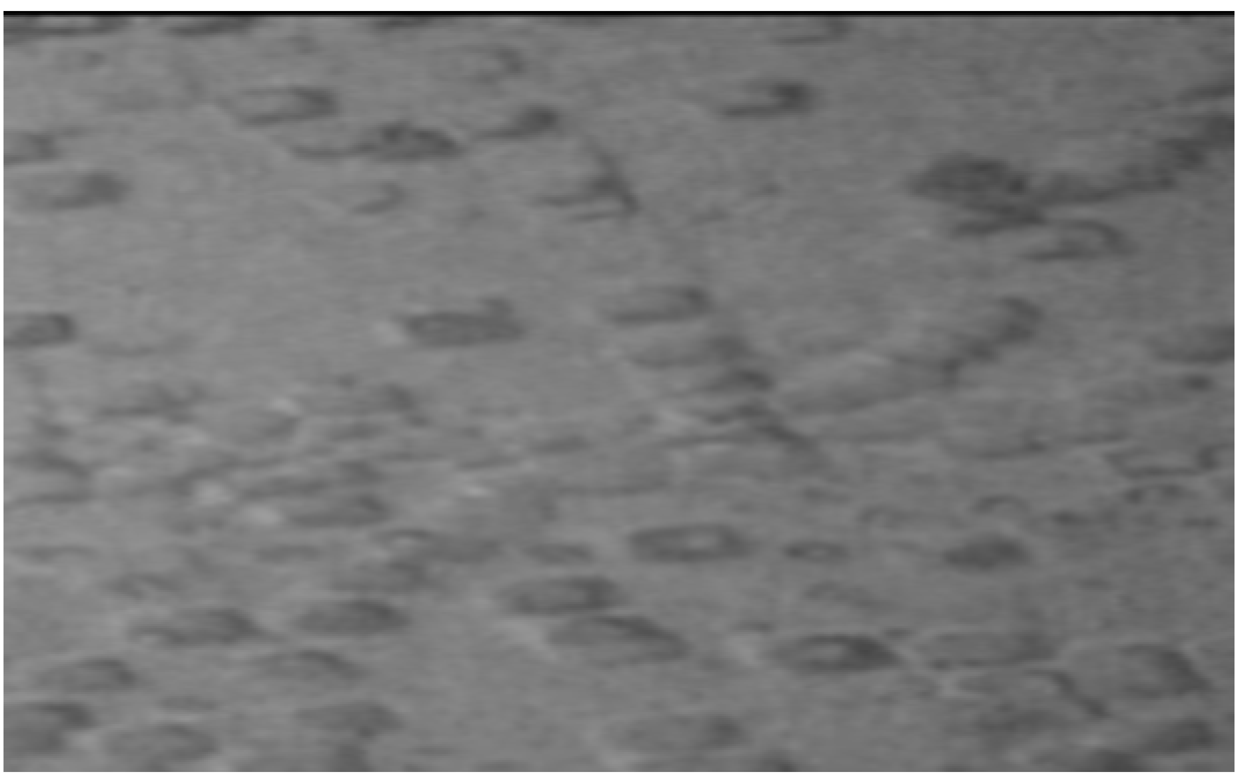

Figure 7

Pure KCl surface dislocations image based on etching analysis

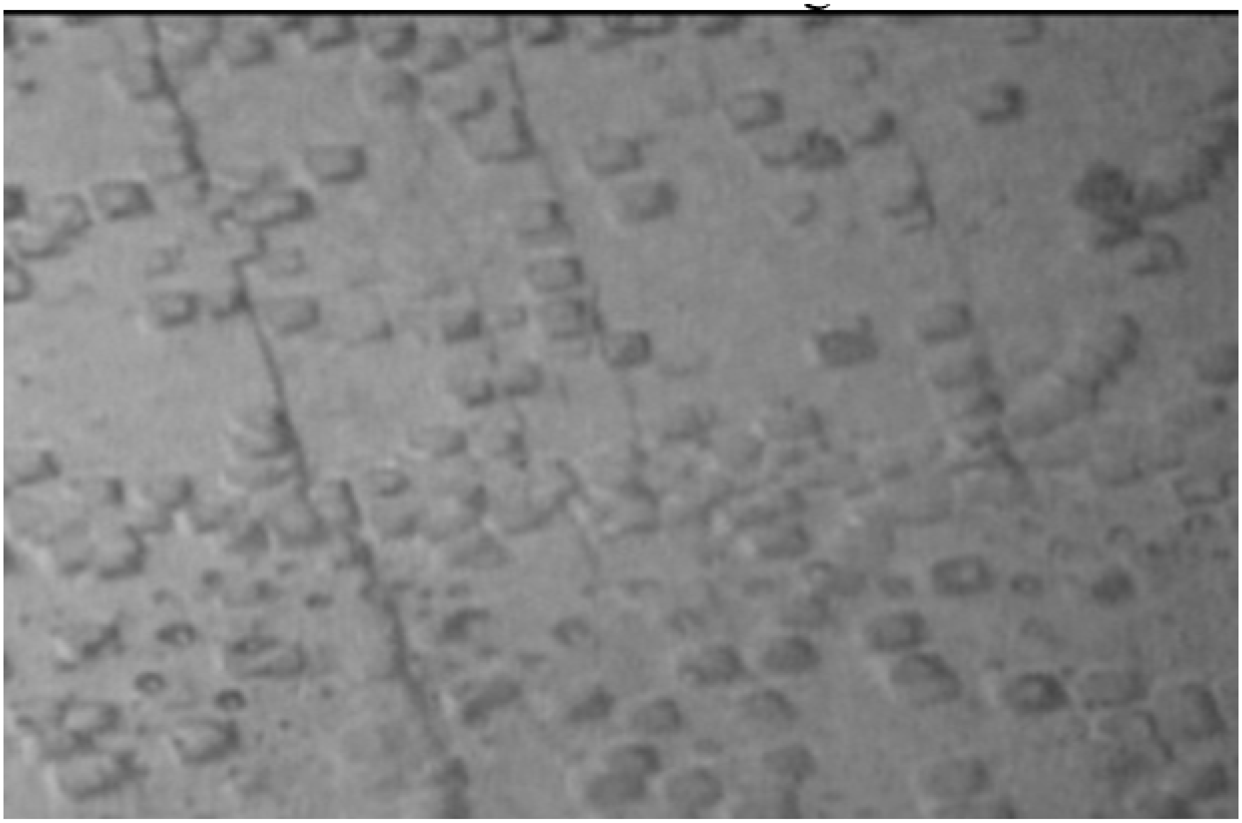

Figure 8

KCl+ 0.5% ND surface dislocations image based on etching analysis

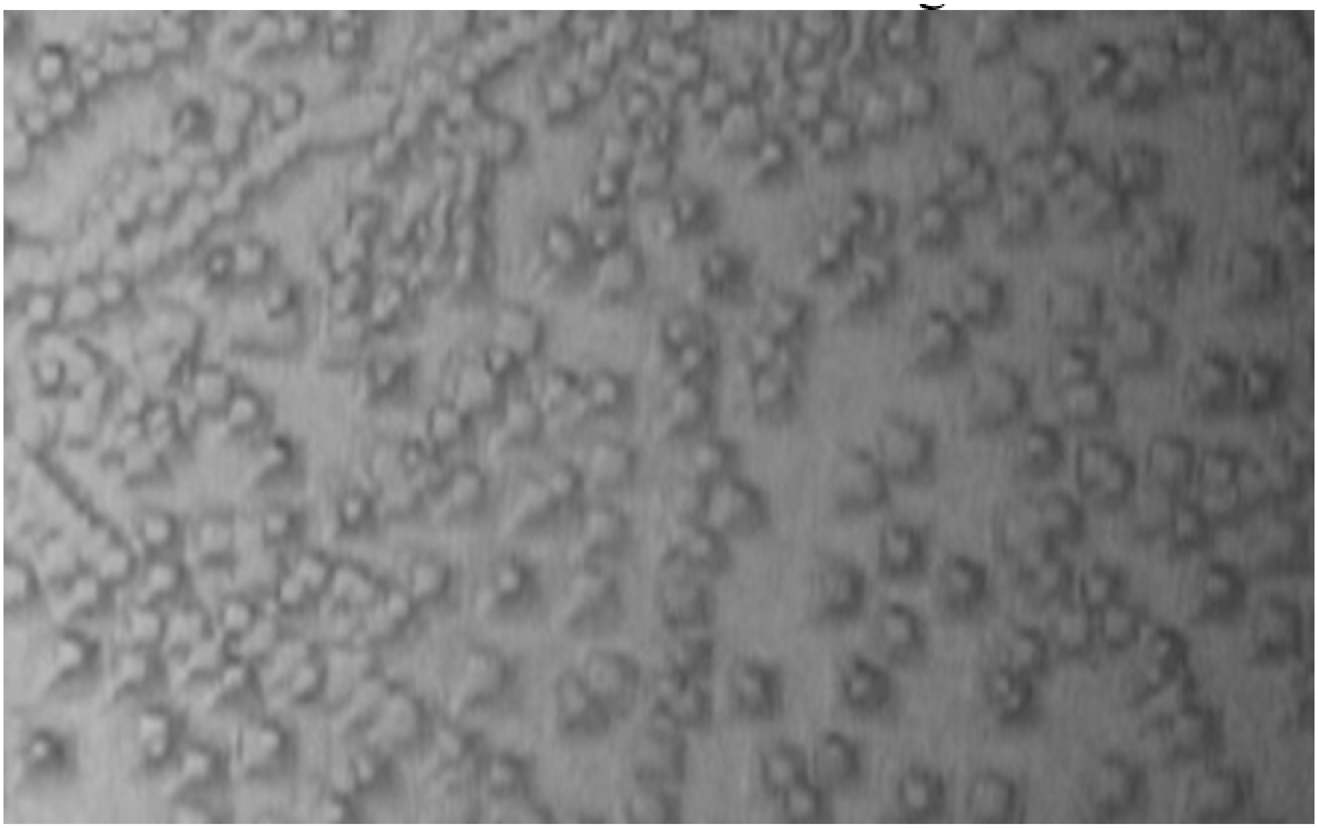

Figure 9

KCl+ 1.0 % ND surface dislocations image based on etching analysis

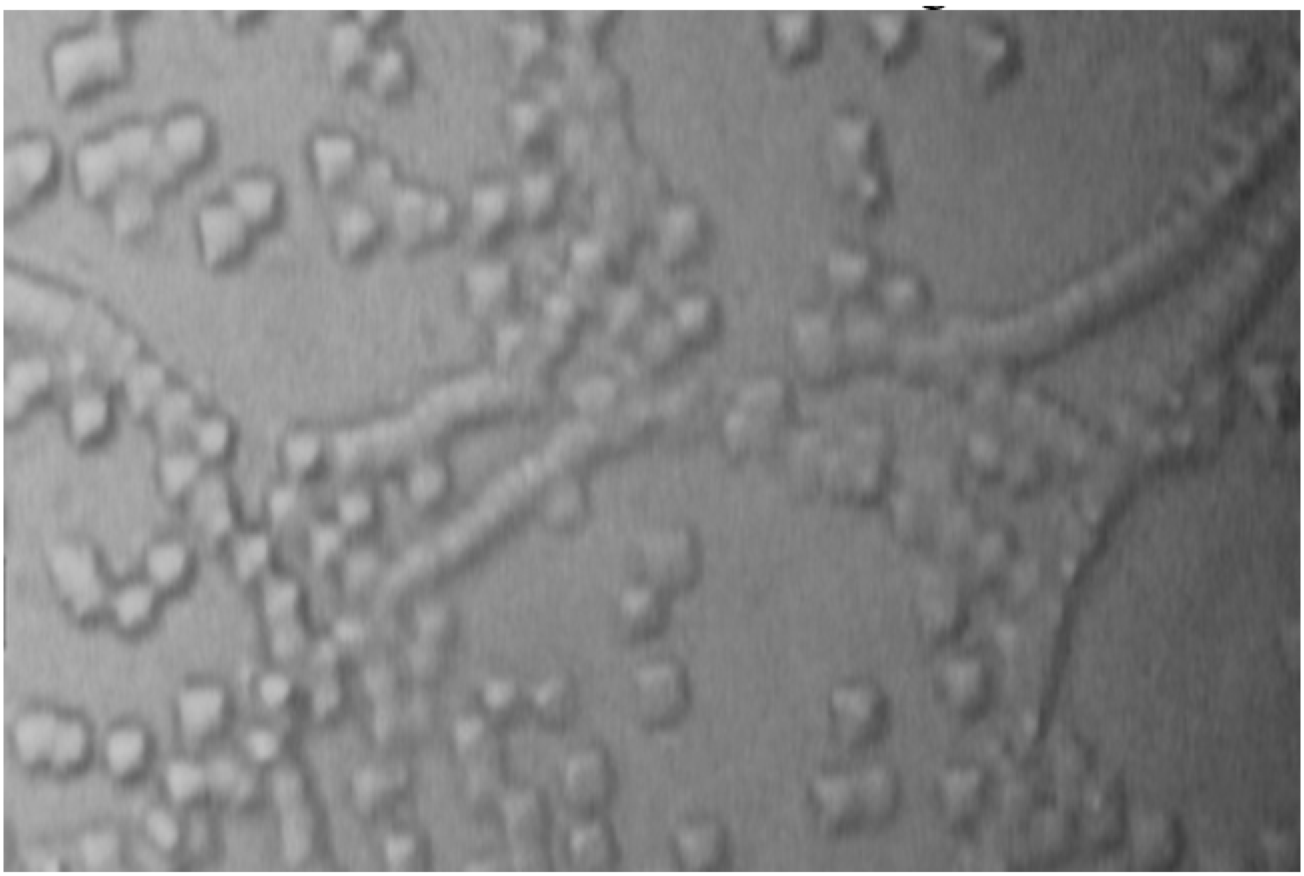

Figure 10

KCl+ 1.5 % ND surface dislocations image based on etching analysis

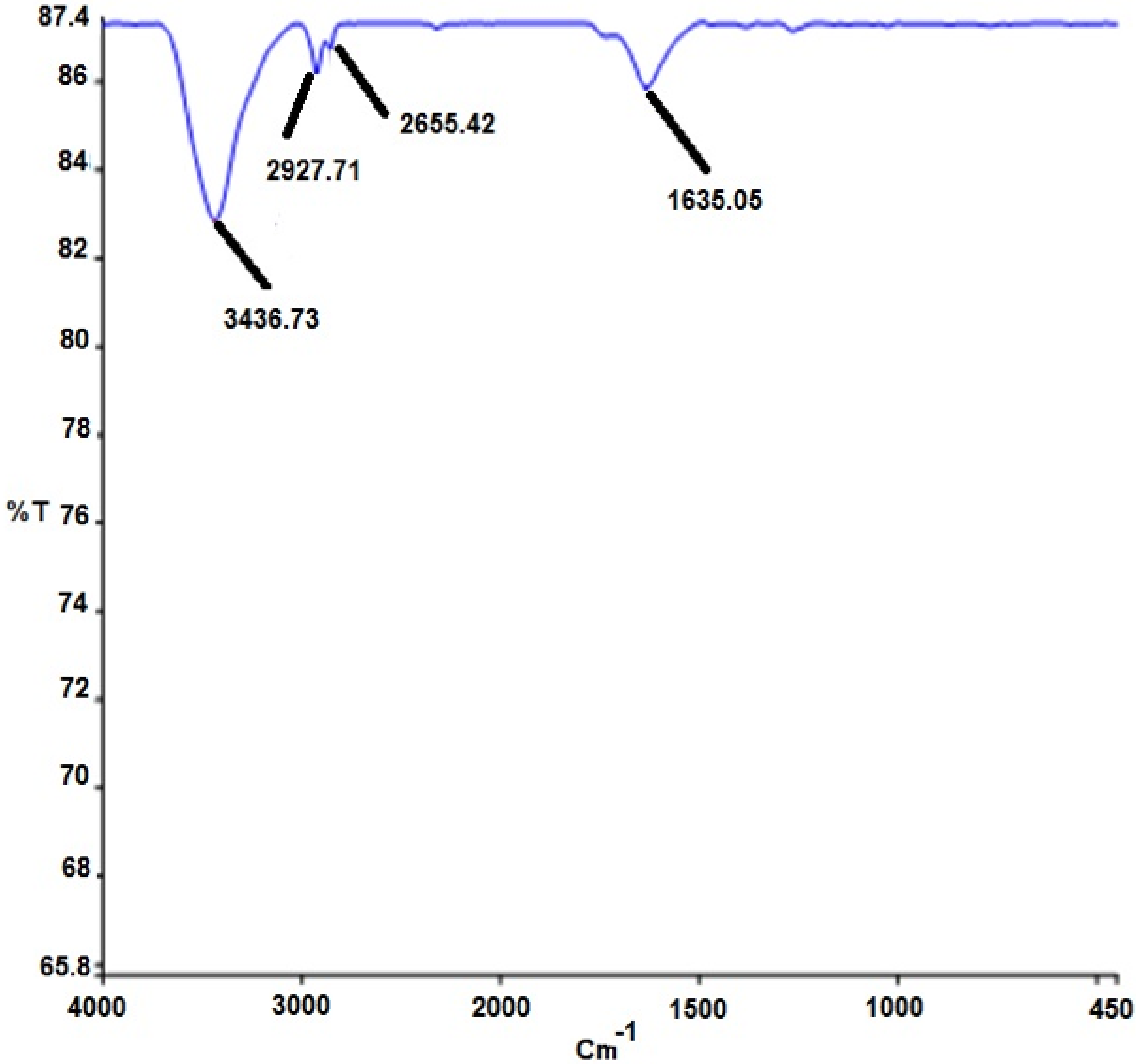

Figure 11

KCl+ 1.5 % ND FTIR transmission spectrum

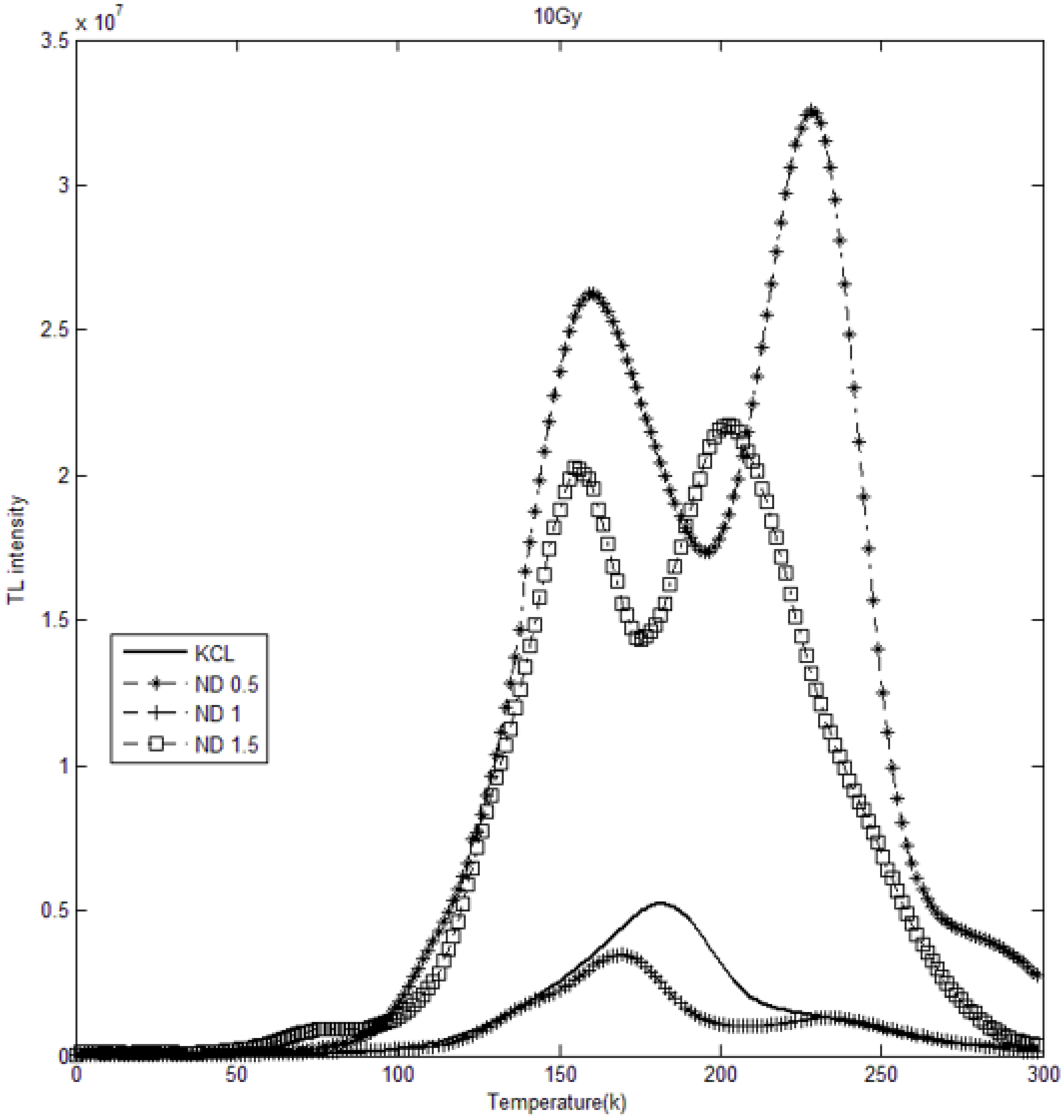

Figure 12

TL curves for the pure KCl, KCl + 0.5% ND, KCl + 1% ND and KCl + 1.5% ND irradiated by 10Gy gamma irradiation

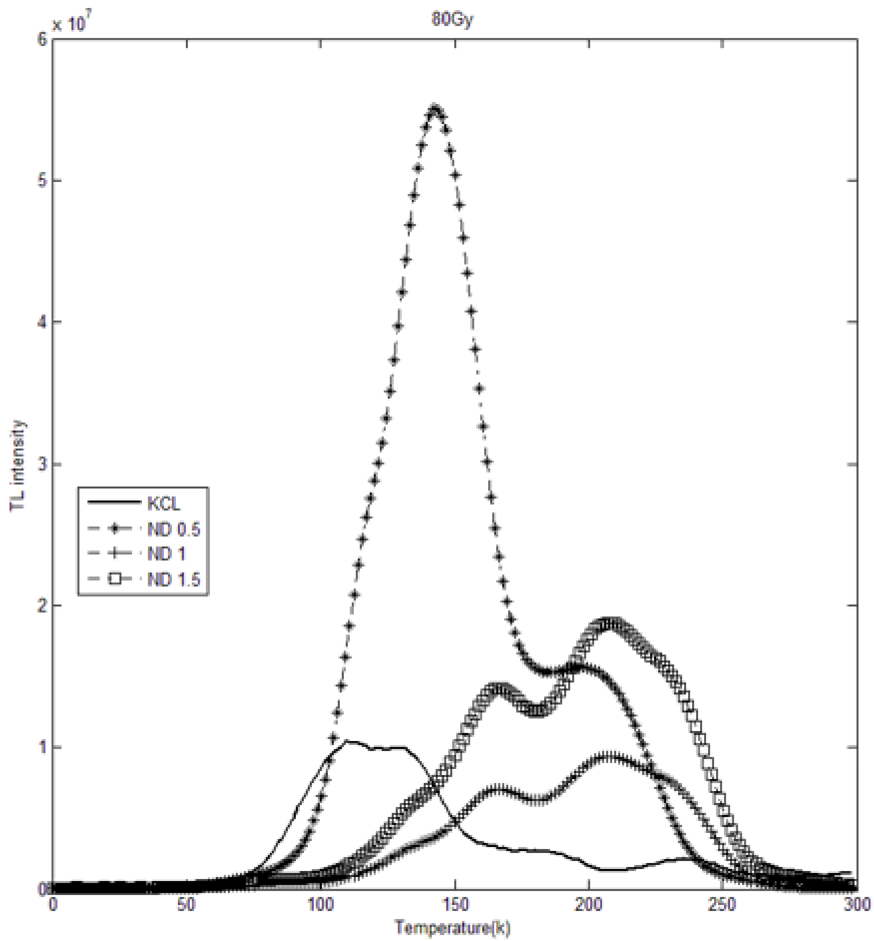

Figure 13

TL curves for the pure KCl, KCl + 0.5% ND, KCl + 1% ND and KCl + 1.5% ND irradiated by 80Gy gamma irradiation

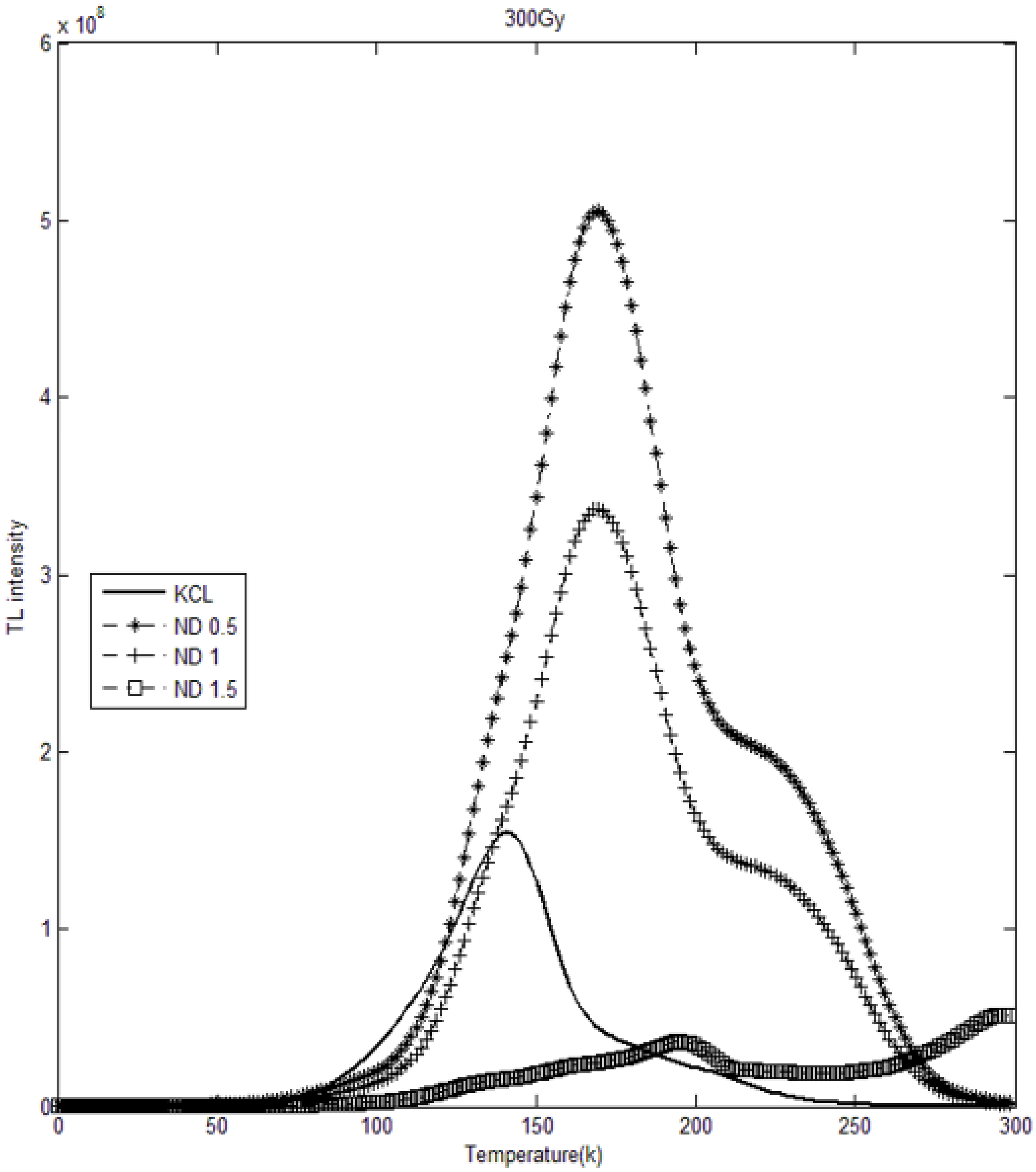

Figure 14

TL curves for the pure KCl, KCl + 0.5% ND, KCl + 1% ND and KCl + 1.5% ND irradiated by 300Gy gamma irradiation

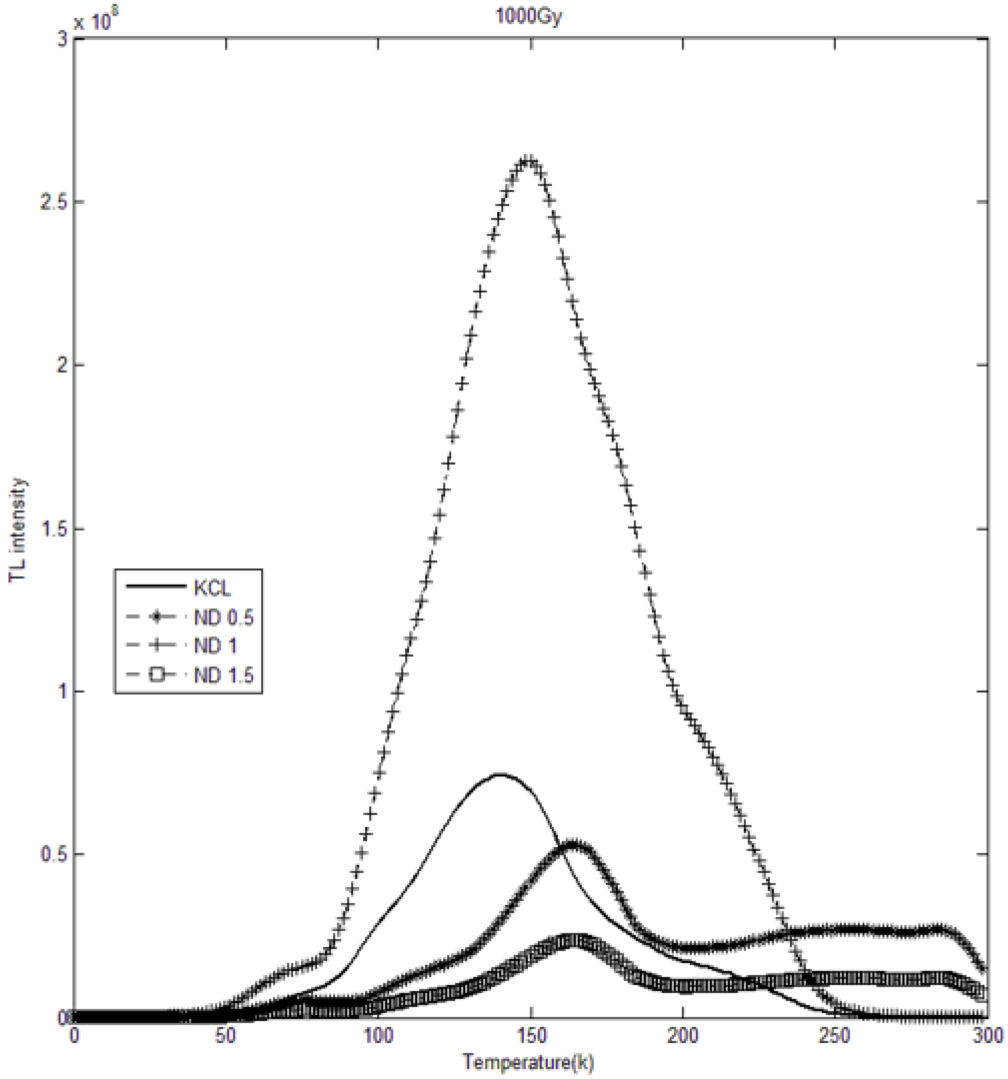

Figure 15

TL curves for the pure KCl, KCl + 0.5% ND, KCl + 1% ND and KCl + 1.5% ND irradiated by 1kGy gamma irradiation